SORPTION AND RELEASE OF STRONTIUM-89 AND

CESIUM-137 BY RECENT SEDIMENTS OF

THE GUADALUPE RIVER OF TEXAS

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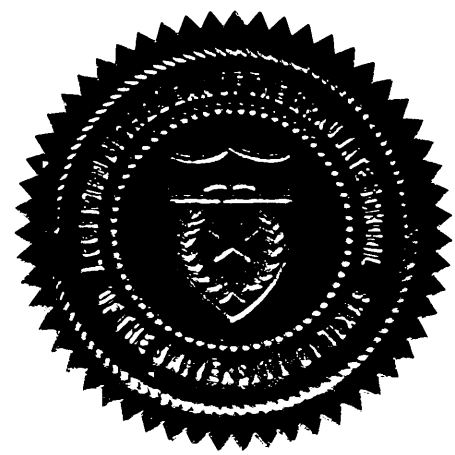

SORPTION AND RELEASE OF STRONTIUM-89 AND CESIUM-137 BY RECENT SEDIMENTS OF THE GUADALUPE RIVER OF TEXAS

by

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DISSERTATION

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Stream transport is an important process in the dispersion of radioactive material that has been released by man into his environment. Some portion of the radionuclides that enter the stream system may remain in solution. However, a significant amount will become associated with aquatic organisms and sediments in the stream. The relative distribution will depend upon the particular radionuclide and the environmental factors of the stream system.

Contemporary sediment samples from preselected locations in the Guadalupe River drainage basin were analyzed for their mineral composition, ion exchange capacity, and radionuclide sorption. The clay minerals were the most significant agents in the radionuclide sorption processes. X-ray diffraction patterns of the clay-sized particles show the presence of a heterogeneous mixed-layered clay mineral complex of poor crystallinity. The degraded nature of these crystallites is suggested by the low intensities and the broad and diffuse diffraction maxima.

Ion exchange capacity measurements gave values of 10 to 47 meq/100 grams and projected values of 20 to 73 meq/100 grams of clay material. Radionuclide sorption studies using cesium-137 and strontium-89 were made on the naturally occurring sediments and sediments from which the organic fraction had been removed. Sorption values were compared with mineralogy and ion exchange capacity to obtain points of correlation.

Rates of radionuclide sorption and release were highest during the first few moments of contact, but totals slowly continued to increase throughout the seven-day duration of the experiments. Sediments containing the naturally occurring organic fraction had the highest sorption values both for strontium-89 and cesium-137. The organic fraction contributes to the over-all sorption capacity of the sediments, even though some of the organic molecules may block exchange sites on the clay minerals against exchange with the radionuclide.

These laboratory experiments indicated that radionuclide sorption in the dynamic fluvial environment was temporary. When the contaminated sediments were placed in conditions simulating a marine environment, 43 percent of the cesium-137 and 42 percent of the strontium-89 were released because of competition for the exchange sites from the more abundant ions in sea water.

Even though fluvial releases are considered an acceptable means of radionuclide disposal, it should be emphasized that all stream systems are dynamic, and this disposal is at best temporary.

The brief respite gained today may be overshadowed by the ultimate contamination of tomorrow.

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INTRODUCTION

Although radioactive waste that is released into man's environment is dispersed by atmospheric circulation and surface hydrology, it will ultimately accumulate in the oceans. Stream transport is one of the many important steps in the dispersion of material at the earth's surface. The problems that arise in the fluvial cycle with respect to movement of radioactive waste necessitate two major considerations:

1. The capacity of a given stream to receive and transport radionuclides without infringing on the water uses; and
2. The determination of the areas of radionuclide accumulation.

Discharge is the controlling factor in the capacity of a stream to transport radioactive waste. However, environmental variations within the stream system are so intimately interwoven with stream discharge that it is impractical to separate the two factors for discussion.

Purpose

Many elements are worthy of consideration in a study of the passage of radionuclides through the environment of man. There are, however, two fission products of particular interest: strontium-90 with a half-life of twenty-five years and cesium-137 with a half-life of thirty-three years. These radionuclides are of major concern to man, not only because of their half-life, but also because of their ability to substitute for similar group elements in body processes.

Because strontium easily substitutes for calcium, the radionuclides of strontium accumulate in the bone tissue. Cesium readily proxies for potassium and therefore accumulates in the body tissue. These radionuclides and others are concentrated to varying degrees by different participants in man's ecosystem. Man, in his position at the top of the food web, obtains the full effects of radionuclide concentrations that have built up in the lower members of the food chain.

The purpose of this investigation was to consider one facet of this complex problem, the sorption of cesium-137 and strontium-89 by sediments in fluvial and lagoonal environments in a climate and topography characteristic of the Southwestern United States.

The area selected for this investigation was the drainage basin of the Guadalupe River of Texas (Fig. 1 and 2). This area was selected because of its accessibility, its freedom from large-scale municipal and industrial waste, and its varied geologic and environmental conditions.

This research is part of a series of studies concerned with the mechanism of uptake and release of radionuclides by sediments in fluvial and marine environments (Reynolds and Gloyna 1963; Patterson and Gloyna 1963; Story and Gloyna 1963; Bolch and Gloyna 1963; Clanton and Reynolds 1963; Clanton and Gloyna 1964; Shih and Gloyna 1966, and 1967).

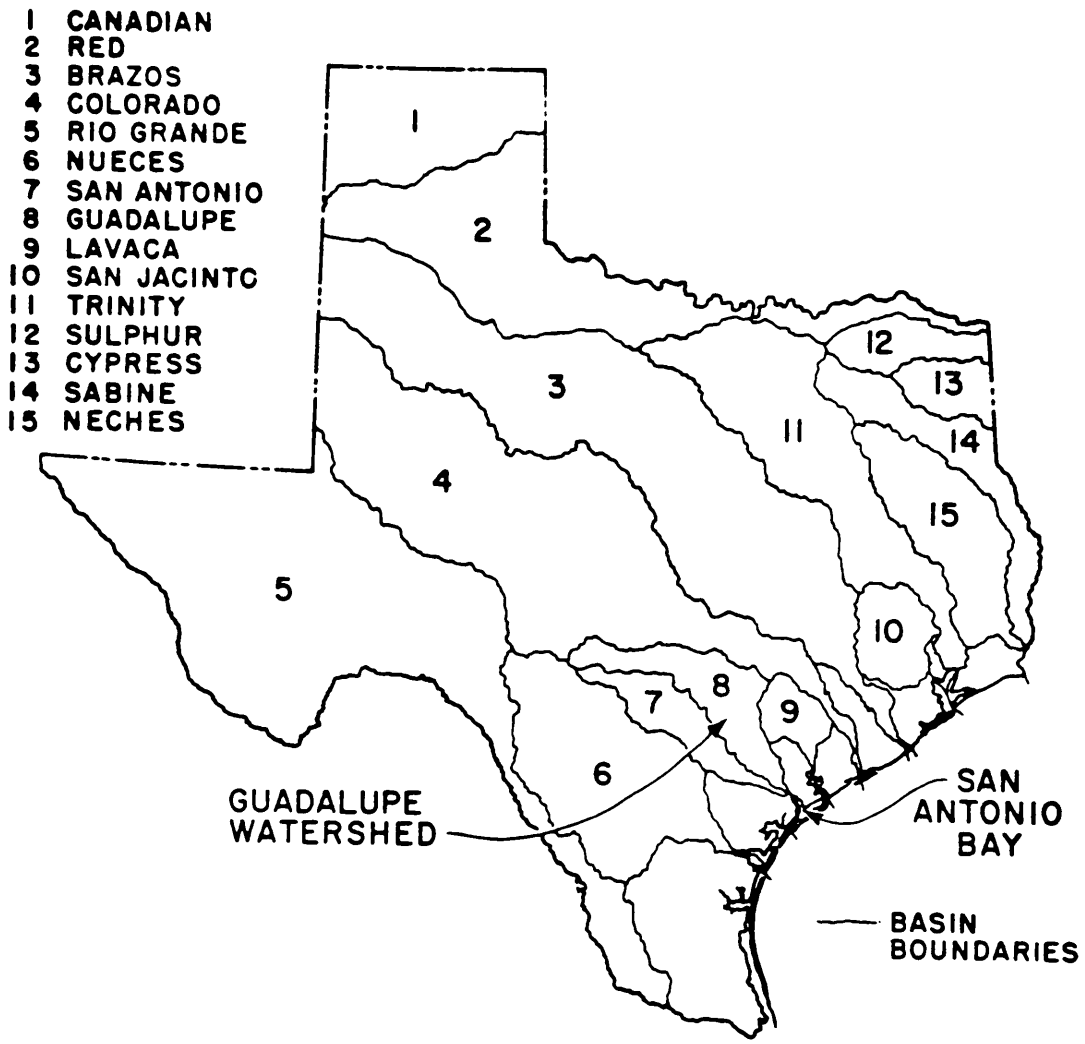

FIG. 1. WATERSHEDS OF TEXAS.

Review

The disposal of radioactive waste presents a unique problem since there is no known agent except time for neutralizing the radioactivity. Radioactive decomposition is not accelerated by the usual physical, chemical, or biological processes. The controlling factor is the inherent rate of decay of a particular radioactive isotope; half-life may vary from a fraction of a second to billions of years. Because man is unable to detect radioactivity directly by the human senses, he must rely on his ingenuity with instruments for detection. Because of this dependence, he is particularly vulnerable to radiation hazards.

Sources of radioactive materials include naturally occurring deposits, fallout from nuclear weapons testing, waste from nuclear fuel processing plants, nuclear power reactors, and from the use of radioisotopes in industry, medicine, and research.

There are only two alternatives (Straub et al. 1956, p. 25) possible for the control of radioactive waste distribution:

1. Dilution of the radionuclide to a level compatible with man's environment.
2. Concentrating the radionuclide with subsequent storage out of the environmental contact of man.

Ideally the short-lived radioactive material that is not dangerous to man's ecologic system could be disposed of by dilution methods. The radioactive material that would affect man and especially the long-lived radioactive isotopes should be concentrated and stored.

The economics of such disposition, however, usually dictates some release into man's environment. Costs of controls are balanced against the possible harmful effects on man.

Maximum permissible radionuclide concentration (MPC) limits for drinking water are currently defined by Handbook 69 of the National Bureau of Standards (1959). Many studies, however, have shown that although the radionuclide concentration may be well below the recommended MPC for drinking water, sediments and biological systems may selectively remove the radionuclide until hazardous concentrations exist (Sayer et al. 1959).

Davis et al. (1958, p. 11) present data showing that significant quantities of the various radionuclides discharged in the effluent from the Hanford reactors were concentrated in the bodies of most organisms that had access to the contaminants via the natural food web.

Pendleton and Hanson (1958, p. 6) observed that some aquatic animals increased their total body concentration of cesium-137 in excess of one hundred times during an exposure period of only two hours. The flesh of waterfowl feeding on a contaminated community contained cesium-137 concentrations of up to six thousand times the cesium-137 concentrations in the water. Carp grown in water having an equilibrium level of 1.5×10^{-3} μc/ml of cesium-137 had a concentration of 4.5 μc of cesium-137 per gram of flesh; twenty grams of this flesh would contain the maximum permissible cesium-137 body burden for man (Pendleton and Hanson 1958, p. 7).

One of the methods for handling large volumes of water containing radionuclide waste involves the use of seepage pits. Cowser et al. (1958, p. 6) report that the intermediate level radioactive waste at Oak Ridge National Laboratories is processed by pumping it through a series of one-million gallon pits excavated in the Caunasauga shale. During the period from June 1952 through December 1957, 8.6 million gallons of waste containing about 112,000 curies of beta activity were released into the pits. As a result of precipitation, sorption by clays, dilution by rainfall, and radioactive decay, 70-80 percent of the cesium and ruthenium, 94 percent of the strontium, and all of the rare earths were removed from the effluent.

These results are supported by the later work of Jacobs and Tamura (1960, p. 207) regarding the use of the Caunasauga shale in the decontamination of intermediate-level waste before it was released into the fluvial environment. Results obtained by Sorathesn et al. (1960, p. 5) also showed that sediment from the Clinch River removed from 80 to 99 percent of radionuclides present in the prepared master solutions.

The increasing concern over the lack of control that can be exercised once the radioactive waste has been discharged into the seepage pits has been expressed by Struxness et al. (1960, p. 78). Although this is an accepted method of disposal, the problems of accidental releases that overflow into the natural stream system and of soil and ground contamination have caused some investigators to question the continued use of the method.

Struxness et al. (1960, p. 45) have raised two questions that may serve as an impetus for continued research:

1. What is the effect of long term radioactive contamination of fresh water environment?
2. What is the capacity of fresh water environment for a continuous input of large volumes of low-level radioactive wastes?

Acknowledgments

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The contribution of Tom Reynolds, my co-worker on this project, is indeed great; his assistance in the drudgery, in the formulation of ideas, in the collection of samples and in the development of

laboratory techniques is sincerely appreciated.

Acknowledgment is also made to the late Dr. E. J. Weiss for his many and varied discussions, his advice and counseling during some of the more trying times; to Dr. Haydn H. Murray and the Georgia Kaolin Company who so generously supplied financial assistance during this period and to Mr. Ray Childress of the Texas Parks and Wildlife Department who aided in the collection of the samples in San Antonio Bay.

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EXPERIMENTAL PROCEDURES AND TECHNIQUES

Sample Collection

Sediment samples were obtained by skindiving or by using an Ekman dredge. Most samples from the Guadalupe River were collected by skindiving. Because of the shallow headwaters of the Guadalupe River drainage basin, skindiving for the samples was not always required. In some instances the river was only a few feet deep. Diving was required only for the filling of the sample container in the deeper waters.

In the deeper waters of the Guadalupe River, repeated dives were made to the river bottom to determine the area or areas covered by fine-grained sediments. When a suitable area had been determined, the diver filled an eight-ounce wide-mouth jar with the fine-grained sediments. The container was capped and marked with sample number and sample location.

Samples from the San Antonio Bay area were collected with an Ekman dredge using the boat furnished by the Texas Parks and Wildlife Department. At predetermined sites, the boat was halted, and the Ekman dredge was lowered to the muddy bottom. By dropping a messenger down the recovery line, the spring-loaded jaws were released, and the dredge was closed. After the dredge was pulled to the surface, the top doors were opened and the recovered sediment placed in sample containers.

Figure 2 is a map of the Guadalupe River drainage basin showing sample locations. This figure shows the location of all samples taken

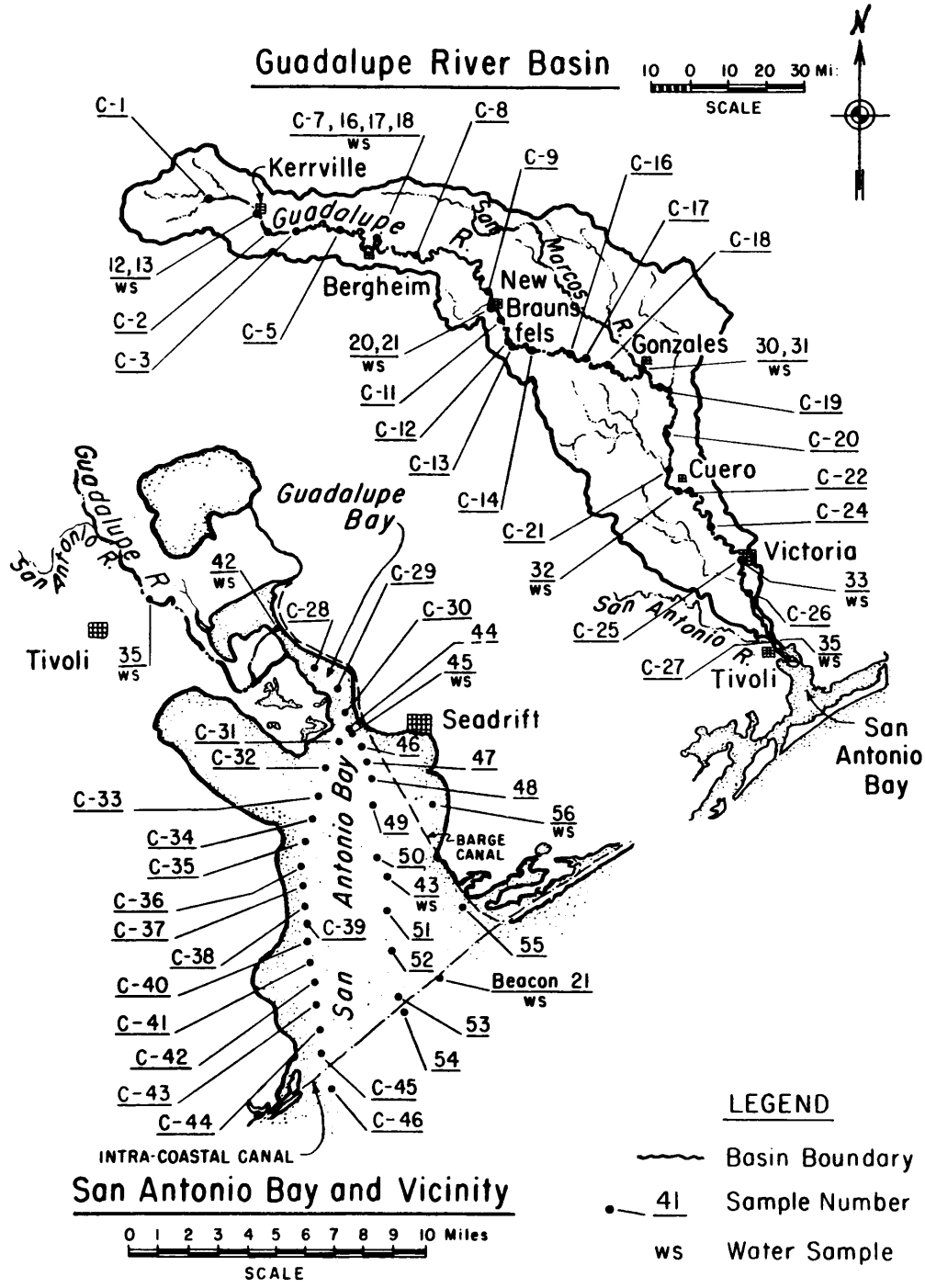


FIG. 2. GUADALUPE RIVER WATERSHED AND SAN ANTONIO BAY.

for the research by Clanton and Reynolds (1963). The original idea was to collect sediment samples from each locality at which the river crossed a major geologic unit (Fig. 3) as recognized by differences in lithology.

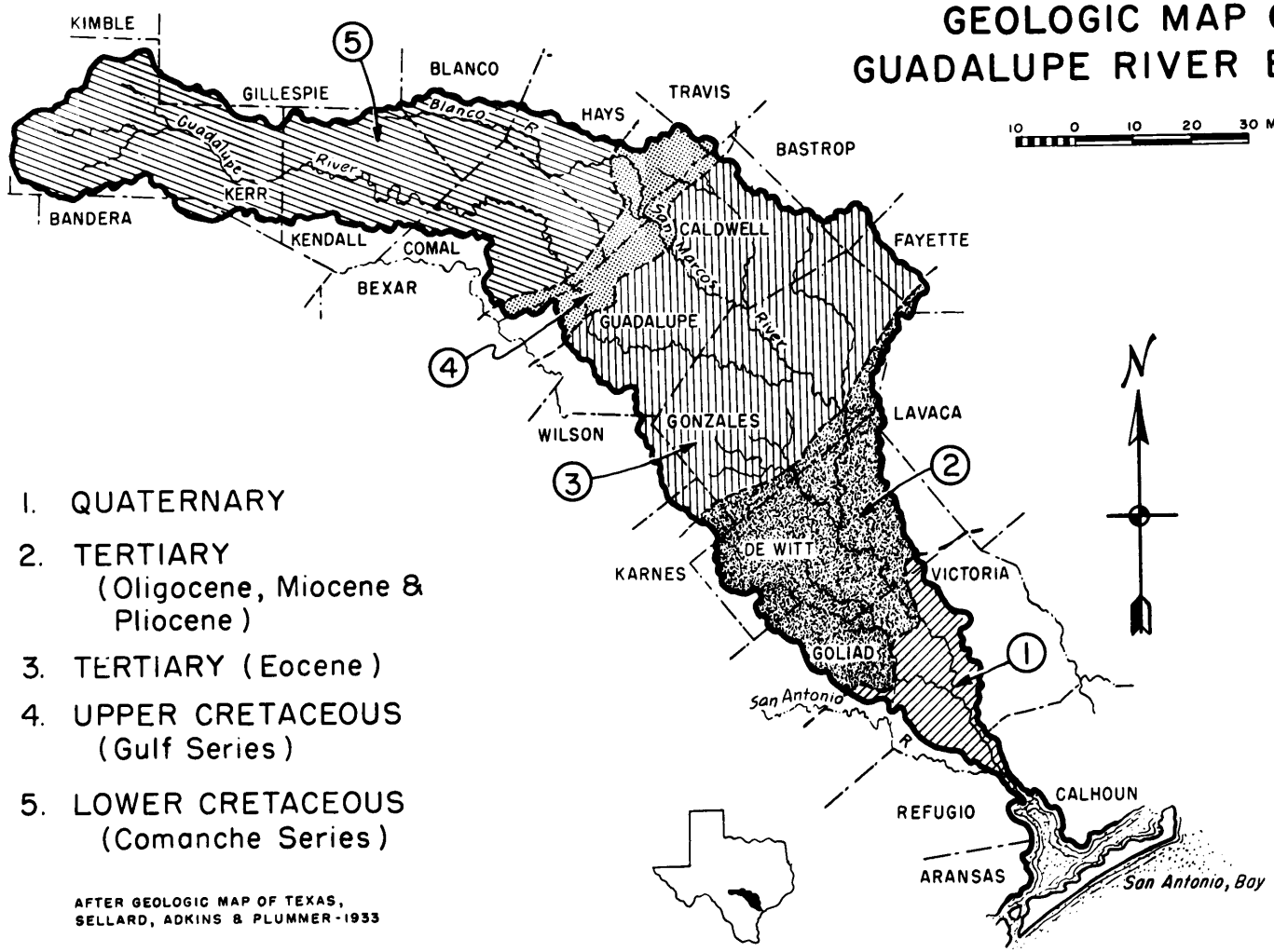
Literature reviewed prior to the initiation of this project placed much significance on the activity of clay minerals as a concentrator of radionuclides. The various lithologies in the Guadalupe River Basin offer a variety of shales, marls, and altered volcanic ash deposits interlayered with sandstones and limestones. The successive lithologies of argillaceous sediments cropping out in the area made the Guadalupe River Basin look most attractive as a study area. The appendix lists the sample locations and indicates the underlying formation where each was collected.

Only after the collection had been completed and most of the samples examined by x-ray diffraction analysis was it realized that the clay-size sediment load of the Guadalupe River was almost completely derived from soil and that degradation of the parent clay material during weathering had rendered specific identification impossible.

Sample Preparation

Fractionation. The sediment samples were oven dried at 60°C, disaggregated by hand and then sieved to separate the less than 325 mesh material from the larger-grained sand and silt. Most of the bed load of the Guadalupe River is sand and silt. Only by fractionating could a reasonable amount of clay-sized material be obtained.

FIGURE 3.
GEOLOGIC MAP OF GUADALUPE RIVER BASIN



The less than 325 mesh material was resuspended and centrifuged to obtain a silt-clay separation of the sediment. A comparison of data with later studies indicated that this fractionation had extracted particles with an equivalent spherical diameter of less than ten microns.

During the preliminary stages of this investigation, several attempts were made to enrich the fractionated sample in clay mineral content by collecting below smaller and smaller equivalent spherical diameters. Samples C-19 and C-36 were fractionated to obtain a greater than 0.5 micron and a less than 0.5 micron size separation. X-ray diffraction patterns of the less than 0.5 micron separation still showed the presence of calcite and quartz. Because the x-ray diffraction patterns were so similar to the x-ray diffraction patterns shown in this report, the effort expended in the second fractionation did not justify the slight increase in quality.

Oxidation of Organic Matter. Although a variety of methods for removing organic material from clays has been reported in the literature, the method used in this research was modified from a technique described by Anderson (1961). This technique, which uses sodium hypochlorite as an oxidizing agent, has the ability to oxidize organic material in the presence of carbonates. Because all of the samples investigated for this report contained from ten to forty percent carbonate minerals, such a technique was required.

An eight milliliter aliquot of five percent sodium hypochlorite solution adjusted to pH 9.5 was added to each four-gram sample of

fractionated sediment in a fifty-milliliter cellulose nitrate centrifuge tube. The tube was then placed in a boiling water bath for fifteen minutes, removed from the bath, allowed to cool, and centrifuged. The Type SS-4 Servall Superspeed Centrifuge was operated at 2000 rpm (Relative Centrifugal Force, RCF-4800) for fifteen minutes. The supernatant solution was decanted and the treatment of the sediment repeated twice.

Barium Saturation. After the supernatant from the third centrifugation was decanted, the samples were saturated with barium for determination of ion exchange capacity. A twenty-milliliter aliquot of 1 N barium chloride solution was added to the sample in the centrifuge tube. The sediment was stirred until well dispersed and then placed in a mechanical shaker for thirty minutes. The shaking machine has a cyclic rate of 450 cpm with a half-cycle travel distance of one inch.

The tubes were removed and centrifuged for fifteen minutes at 2000 rpm (RCF-4800). The barium solution was decanted and the treatment repeated four times.

Elution. After the fifth centrifugation in the barium saturation procedure, the sediment samples were washed thoroughly by repeated dispersions in distilled water and successive centrifugations. As more of the excess barium chloride was removed, the time required to spin down the sediment increased.

The decanted wash solutions were tested for the presence of the chloride ion using a 0.1 molar silver nitrate solution. Excess barium

present in the sample was considered to be removed only after two successive washing solutions showed the absence of a silver chloride precipitate when silver nitrate was added to the decanted solution. Complete removal of excess barium chloride usually required from eighteen to twenty washings.

The centrifuge tubes containing the washed sediment were then placed in an oven and evaporated to dryness at 60°C. When the sediment was dry, the samples were disaggregated by hand and then ground in a Fisher Mortar Grinder to prepare a uniform fine-grained material. This prepared material was then analyzed by an x-ray fluorescence technique to determine the barium exchange capacity.

X-Ray Diffraction

Instrumentation. A General Electric XRD-5 Spectrometer with a No. 3 Pulse Height Selector and SPG-3 Scintillation Counter was used to record all x-ray diffraction data. Nickel-filtered copper K alpha radiation was utilized; operating conditions were 16 ma. at 35 K.V.P. The Pulse Height Selector settings that were most effective for these conditions were E = 9.0 volts and Δ E = 7.0 volts, which correspond to a 9 volt baseline and a 14 volt window.

The ratemeter and strip-chart recorder were operated with a logarithmic response (Log 90) that corresponded to full-scale deflection at 1500 counts per second. X-ray diffraction patterns were normally recorded at two degrees 2θ per minute through the range of 2° 2θ to 38° 2θ . Although many of the calcite, dolomite, and quartz reflections occurred at 2θ angles larger than 38°, once the general

mineralogy of the sample suite was known identification of the various components in a particular sample could be made with a limited number of reflections.

Percentage Determinations. The percentage of non-clay minerals was determined by comparing the x-ray diffraction intensities of quartz and calcite standards with the x-ray diffraction intensities observed from the sediment samples.

The materials used as standards were ground in a Fisher Mortar Grinder until the particles would pass through a 325 mesh sieve. The less than 325 mesh material was then packed in sample holders for intensity determinations. The Log scale setting described above was used to scan each standard.

For actual working curve construction the goniometer was set to the most intense reflection for each standard, and six counts of ten seconds duration were made to determine the average number of counts per second (cps) that could be obtained from the standard. The standards selected averaged 1500 cps for calcite and 1700 cps for quartz. These values were then used to prepare graphs which could be used to scale in direct proportion the percentage of quartz and calcite present in the sampler. Percentages could be read directly from the x-ray diffraction intensities recorded on the strip charts. No corrections were made for absorption coefficients.

Both standards and many of the samples were repacked and rerun several times in order to determine the error that would occur because of variations in packing in the holders. The maximum variation observed

was less than ten percent of the amount of material present. As a check the standards and some of the samples were also analyzed on a second x-ray unit. Percentage determinations on the two units varied no more than did the replicate determinations on the primary unit.

X-Ray Fluorescence

Instrumentation. A General Electric XRD-5 Spectrometer with a No. 3 Pulse Height Selector and SPG-3 Scintillation Counter was used to determine emission data. A platinum tube operated at 50 K.V.P. and 46 ma. was utilized as a radiation source. The optimum Pulse Height Selector settings were E = 4.0 volts and Δ E = 6.5 volts corresponding to a baseline of 4 volts and a window of 13 volts. The ratemeter scale factor was set for a linear response of 2000 cps with an integrated time constant of 1 second.

The purpose of the pulse height selector is to limit the range of pulse energies counted. The baseline setting (E) and the window setting (Δ E) can be set so that only pulses from the counter tube having amplitudes within the range $E \pm \Delta E$ will trigger a constant amplitude pulse, which will be recorded by the scaler, ratemeter and the digital printer. The pulse height selector controls can then be adjusted to accept a discrete range of radiation energy characteristic of a particular element.

X-ray fluorescence is perhaps the most versatile of all analytical chemical methods. Primary x-rays are produced in the tube by electron bombardment of a metallic target (e.g., platinum). The generated white radiation excites electrons of the elements present in the sample.

As other electrons spontaneously fall back into the vacated energy level from a higher energy level, secondary x-rays characteristic of the elements present are emitted. The characteristic line spectrum for an element consists of a series of wave lengths corresponding to the various permitted electron transitions that occur between the electron shells of the excited atoms.

The emission spectrum of an element is a function of atomic number. As the atomic number increases, the wave length of the characteristic line decreases. Because the wave length is inversely proportional to the energy of the radiation, an element with a higher atomic number will produce a higher energy radiation although of shorter wave length than an element with a lower atomic number.

The chemical properties of an element are primarily dependent on the behavior of its outer electrons. It should be stressed that the emission spectrum originates from the inner electrons and is therefore essentially independent of the chemical form and the type of bonding present in the analytical samples.

Exchange Capacity Determinations. The use of barium as an exchange ion is well documented in the literature (Grim, 1953, p. 155, Robinson, 1962, p. 69). The x-ray emission technique was used to determine the barium exchange capacity of the fractionated sediments.

Lithium fluoride (2D-4.028A) was used as an analyzing crystal in the emission technique. The lines used for emission determinations were the K alpha doublet. The entire emission spectrum from 10°2θ to 11.33° 2θ was scanned at 0.2° 2θ per minute and recorded using

a 40 second preset time interval. This region was scanned a total of six times, averaged, and then computed on a count per second basis. The values were then compared with the calibration curve to determine the exchange capacity of the unknown samples.

The calibration curve (Figure 4) was made by the method of addition. The following amounts of $BaSO_4$ were added to a commercial bentonite to make the calibration standards:

grams of $BaSO_4$	grams of clay	meq/100 grams
0	5.000	0
0.1167	5.000	20
0.2334	5.000	40
0.3501	5.000	60
0.4668	5.000	80

The clay and $BaSO_4$ were hand ground, sieved, and then ground again for twenty minutes in a Fisher Mortar Grinder to insure a homogeneous standard.

These prepared samples were scanned for forty seconds at a rate of 0.2° 2Θ per minute through an angle of 10° 2Θ to 11.33° 2Θ. Six scans were made of each standard, the values were averaged and a calibration curve prepared with meq barium vs. number of counts per second (Fig. 4). This gives a line with a slope equal to:

$$m = \frac{\Delta \text{ count}}{\Delta \text{ meq}}$$

where:

m = slope of the line

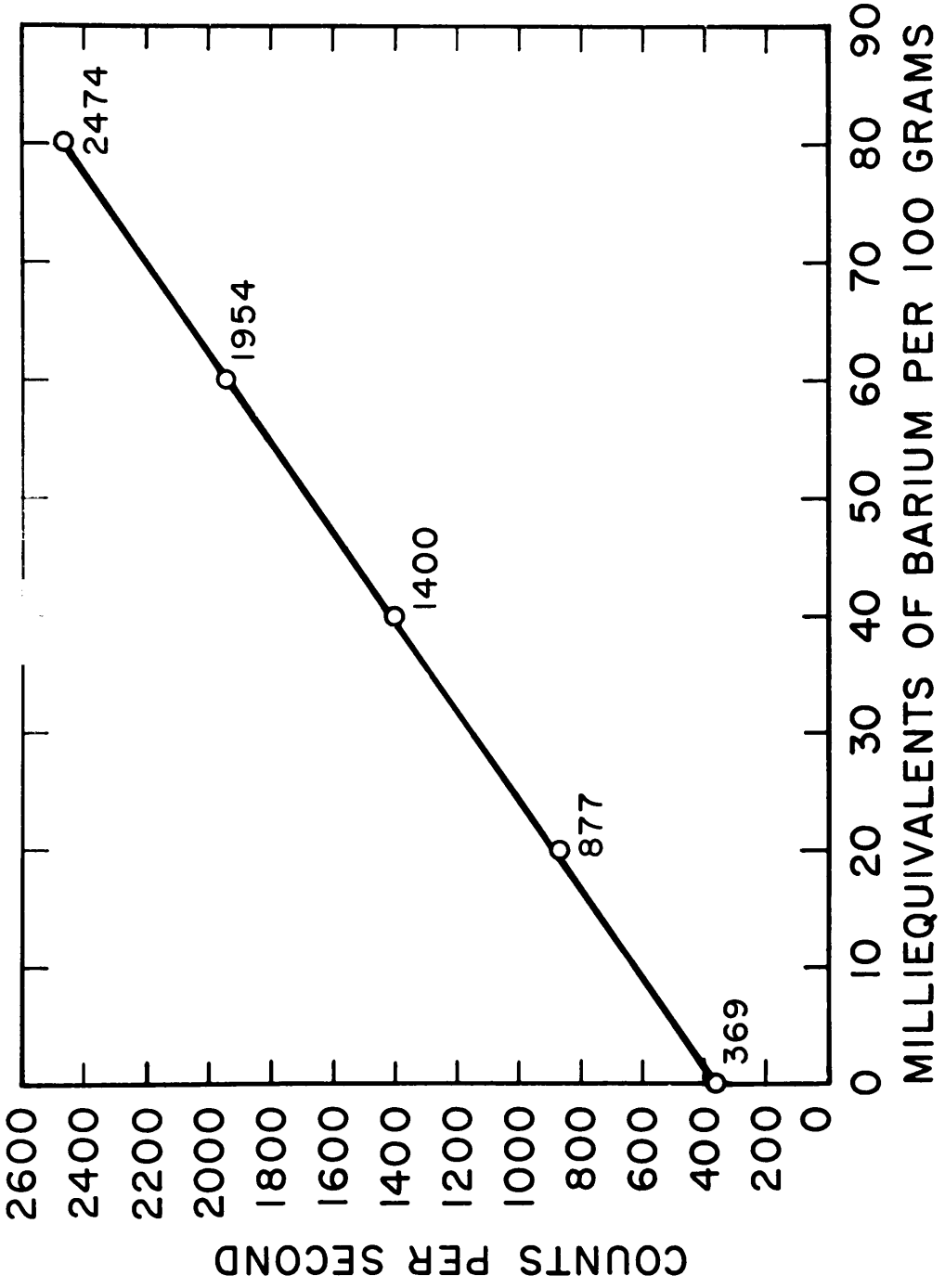


FIGURE 4. CALIBRATION CURVE

meq = milliequivalents of barium per 100 grams of clay

count = average counts per second

Since there will be some background radiation scattering even at zero concentrations of barium, the intercept of the calibration curve with the y axis must be found to complete the equation. This point can be determined by extrapolation from points on the calibration curve, or as was done for this calibration curve, a clay sample without any $BaSO_4$ added to it was analyzed to determine background scattering.

The fluorescence technique requires that the samples used as standards and as unknowns be as similar as possible in grain size and packing. Grain size was controlled by fractionation and grinding; packing was controlled through the use of a Carver Laboratory Press. All samples were pressed to a pressure of 7000 psi in 1 1/8 inch ID chrome steel rings in order to duplicate sample packing.

Eight replicate samples were made for two different specimens. These replicates followed the complete process as previously described.

Each of the replicate samples was counted six times to obtain an average cps value. The eight replicate samples had a maximum variation of plus or minus one percent of the mean for the two specimens that were checked. Because of this reproducibility, none of the other samples was carried in duplicate through the complete process.

Radiation Determinations

Instrumentation. The presence of a radioactive species was detected by a Baird Atomic 750 proportional counting system employing

an end-window, gas flow, 2 pi detection chamber; the unit was also equipped with an automatic sample changing device.

Sorption Studies. Strontium-89 (half-life 55 days) and cesium-137 (half-life 33 years) sorption studies were made on certain samples to determine the effects of mineralogy and exchange capacity on radionuclide sorption. The fractionated sediment samples were divided into two parts. One portion was treated using the sodium hypochlorite technique to remove the organic material present in the samples; the other portion remained in its natural state.

Master solutions of distilled water containing 5×10^{-10} mg/l of strontium-89 and 5×10^{-7} mg/l of cesium-137 without carrier were prepared. Fifty milligrams of sediment and one hundred milliliters of master solution were placed in four-ounce capacity jars. Blanks which contained the test solution, exclusive of sediment, were also prepared.

The bottles were capped and then placed in a reciprocating shaker. After periods of one hour, one day, three days and seven days, the shaking was interrupted, the bottles were removed from the shaker and centrifuged for five minutes at 3000 rpm (RFC 11,000). A one milliliter aliquot of the supernatant solution was withdrawn and placed in an aluminum planchet to be dried and counted. Before the bottles were returned to the shaker, the pH of the solution remaining in the bottle was recorded.

The aliquot samples were evaporated to dryness, and the time required to accumulate 9000 counts was recorded. The gross count was corrected for self-absorption and decay as required. Background counts

were also made and the gross count corrected to take into account the error that accumulated by the varying counting times.

Each set of sixteen samples, the number of specimens processed at a given time, was counted against a cesium-137 standard. The precision of this counting method was determined to be plus or minus one percent.

The amount of cesium and strontium sorbed by the sediments was computed by comparing the initial and final counting rates of the supernatant solution. This technique then determines the amount of radionuclide remaining in solution; a calculation is required in order to determine the amount of radionuclide sorbed by the sediment.

RESULTS

Mineral Identification

Non-Clay Minerals. During the initial stages of this investigation samples were prepared for x-ray analysis as sedimented glass slides. The patterns from this preparation were of poor quality and attempts to improve the diffraction data by the usual heating and glycolation techniques did not produce satisfactory results. The samples were repacked in powder sample holders in an effort to produce the best quality x-ray patterns obtainable. Repeated attempts using various techniques of sample preparation and instrument setup failed to improve the quality of x-ray data over that shown in Figures 6, 7 and 8. These x-ray diffraction patterns were made from air dried powder pack samples.

Figure 5 is a graph showing the separate amounts of non-clay minerals as determined by x-ray diffraction intensities of the fractionated ten micron sediment samples. All fractionated samples contained quartz, calcite, and varying amounts of clay minerals. In addition samples C-1 through C-19 contain minor amounts of dolomite. Calcite is the dominant non-clay constituent in all of the samples, except C-45, with quartz following in a secondary role. The quartz-calcite abundance inversion of C-45 can perhaps be explained by location; samples C-45 and C-46 were collected in the spoil area of the intracoastal canal and probably reflect disturbed sedimentary conditions caused by dredging rather than a natural pattern of sedimentation.

The points plotted on the graph are observed values. The probable

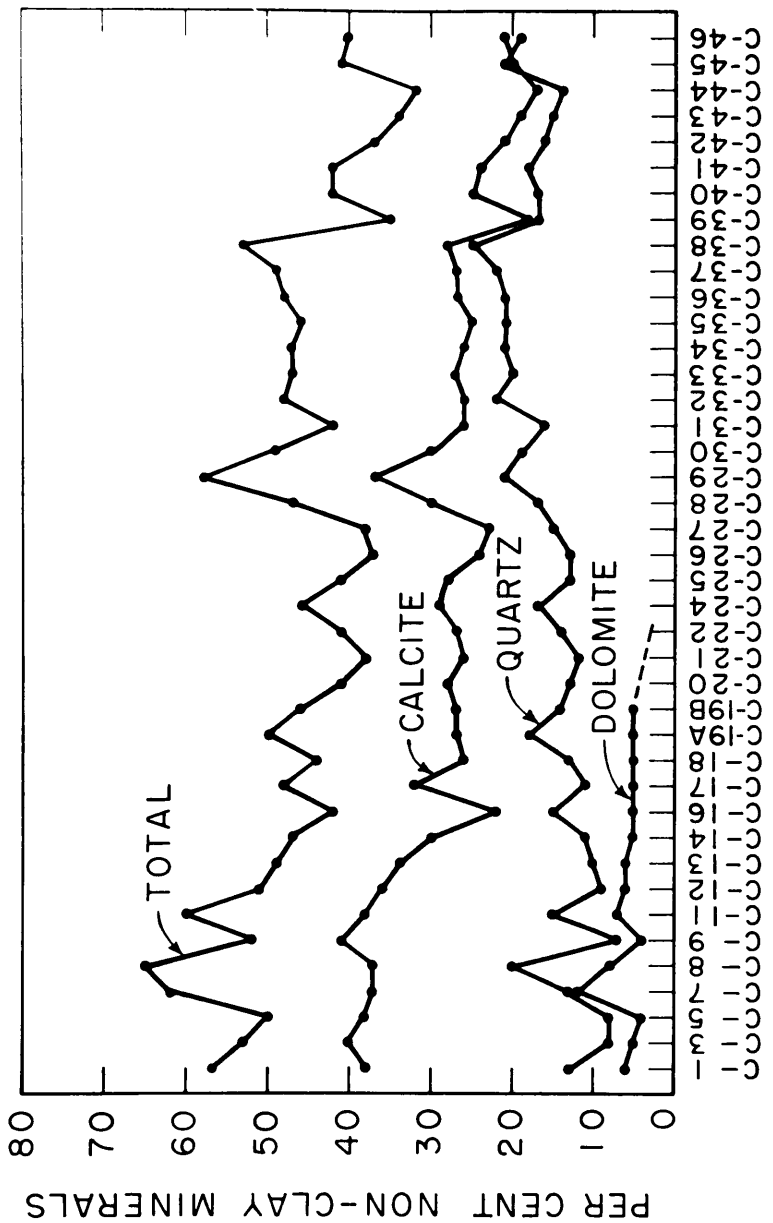


FIGURE 5. NON-CLAY MINERAL PERCENTAGES

range for estimations is considered to be plus or minus ten percent of the reported value. Two general trends are apparent. The calcite content of the sediment decreases toward the coast and toward more saline water in San Antonio Bay. The quartz content increases toward the coast and well into the lagoon environment, then decreases in the more marine environment.

Particle size has a definite relation to the mineralogy of the sediment. Although no attempt was made to determine precise quantitative values, it was noted that an increase in sediment size would increase the relative percentages of quartz, calcite and dolomite.

Figures 6, 7 and 8 are representative x-ray diffraction patterns of the fractionated sediments of the Guadalupe River and San Antonio Bay.

The mineralogy interpreted from the x-ray diffraction patterns is indicated by the following letters; "Q" indicates quartz, "C" calcite, and "D" dolomite. The clay mineral peaks have been left undesignated. These include the maxima in the 15.5-10 A range, discrete features at 10 A and 7 A, and the composite clay intensities observed at 4.4 A and 2.5 A.

The clay-sized contribution from the headwaters of the Guadalupe River is illustrated by sample C-1 (Fig. 6). The sediments containing both the contribution from the Edwards Plateau and the Cretaceous-Tertiary Coastal Plain are illustrated by sample C-19 (Fig. 7). Figure 8 is the x-ray diffraction pattern of sample C-41 and represents the bulk of the clay-sized sediments in the bay environment. These patterns

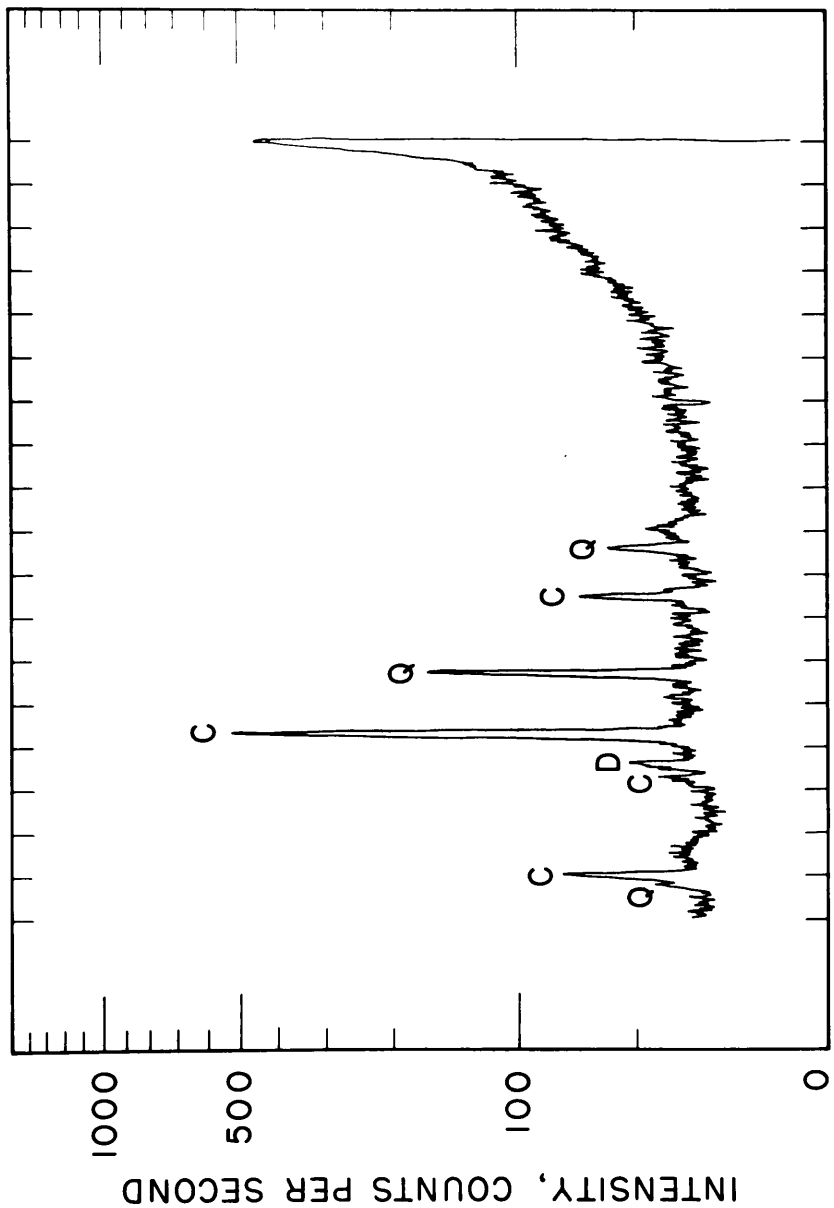


FIGURE 6. X-RAY DIFFRACTION PATTERN OF SAMPLE C-1

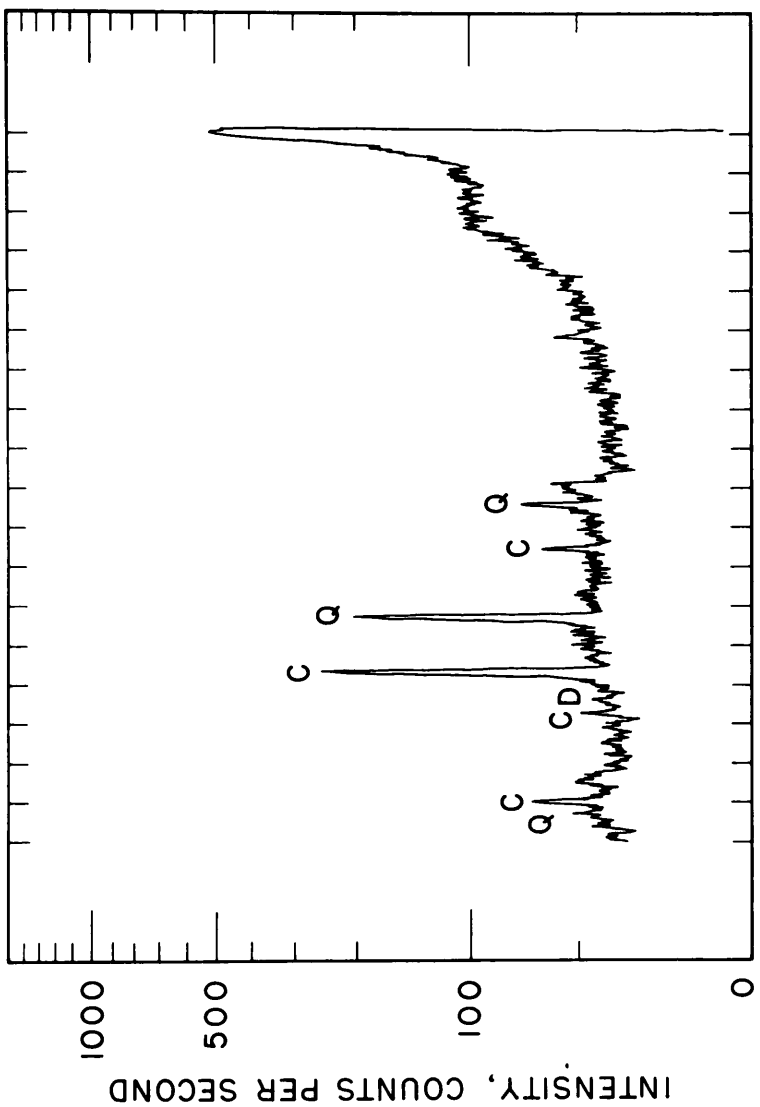


FIGURE 7. X-RAY DIFFRACTION PATTERN OF SAMPLE C-19

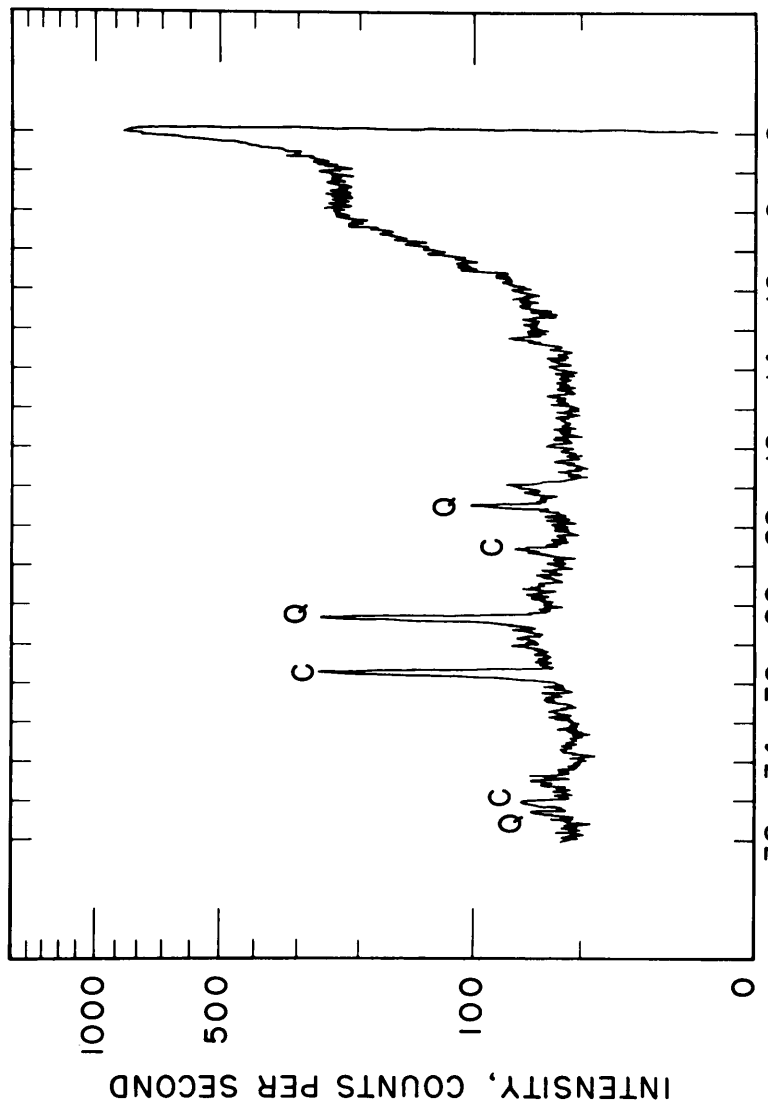


FIGURE 8. X-RAY DIFFRACTION PATTERN OF SAMPLE C-41

also represent the extremes of x-ray diffraction data obtained from the sediments investigated in this study.

Clay Minerals. The clays contained in the sediment samples from the Guadalupe River are weathered materials that have been transported into the stream system after developing by subaerial weathering of the parent rock in the soil zone. The progressive alteration under the influence of weathering has destroyed the well crystallized clay material and left a heterogeneous residue with some expandable layers within the crystallites.

The x-ray diffraction patterns of this material cannot be considered characteristic of a single clay group, i.e., kaolinite, illite, chlorite, or montmorillionite, but are rather a composite diffraction pattern. The basal reflection, which is usually considered to be the most distinctive feature of a clay group, appears as a low diffuse reflection that usually covers the entire 10-15.5 A spacings with more or less equal intensity. Some of the samples have superimposed on this composite basal reflection a minor feature or features that can be attributed to a specific clay mineral group. However, these minor features also show rather broad diffuse reflections not characteristic of well crystallized material.

The asymmetry of the basal reflections and the generally broad character of the other reflections suggest that this material is a mixed-layer clay mineral complex of poor crystallinity. The structure is probably best described as randomly stacked, degraded clay minerals with the c crystallographic direction randomly oriented.

Exchange Capacity

Measured. Ion exchange capacity values were determined by the barium saturation technique. The x-ray fluorescence scan was repeated six times for each sample, averaged and then computed on a count per second (cps) basis for comparison with the calibration curve (Fig. 4).

Ion exchange capacity values varied from a high of 47 to a low of 10 meq of barium per 100 grams for the fractionated sediment samples. Because of the high percentage of minerals without appreciable exchange capacity it was considered necessary to plot exchange capacity and non-clay mineral content on the same graph for comparison purposes.

Figure 9 shows two curves; the lower one is a reiteration of the non-clay mineral total from Figure 5. The top curve is a plot of the measured exchange capacity of the fractionated sediments. Although there are some discrepancies, there is in general a surprising similarity in the two curves. Some irregularities can be smoothed somewhat when the minor features are considered, i.e., the kaolinite and illite content of the sediments, which would have a low exchange capacity.

Calculated. Using the data from Figure 9, it is possible to calculate the average exchange capacity of a clay with properties similar to the one observed for a particular sample. The calculations, however, involve the percentage of non-clay minerals present in the sediments. Because the reported values are known only within an accuracy of plus or minus ten percent of the true value, this error will be carried into the average exchange calculation and will influence the accuracy of the

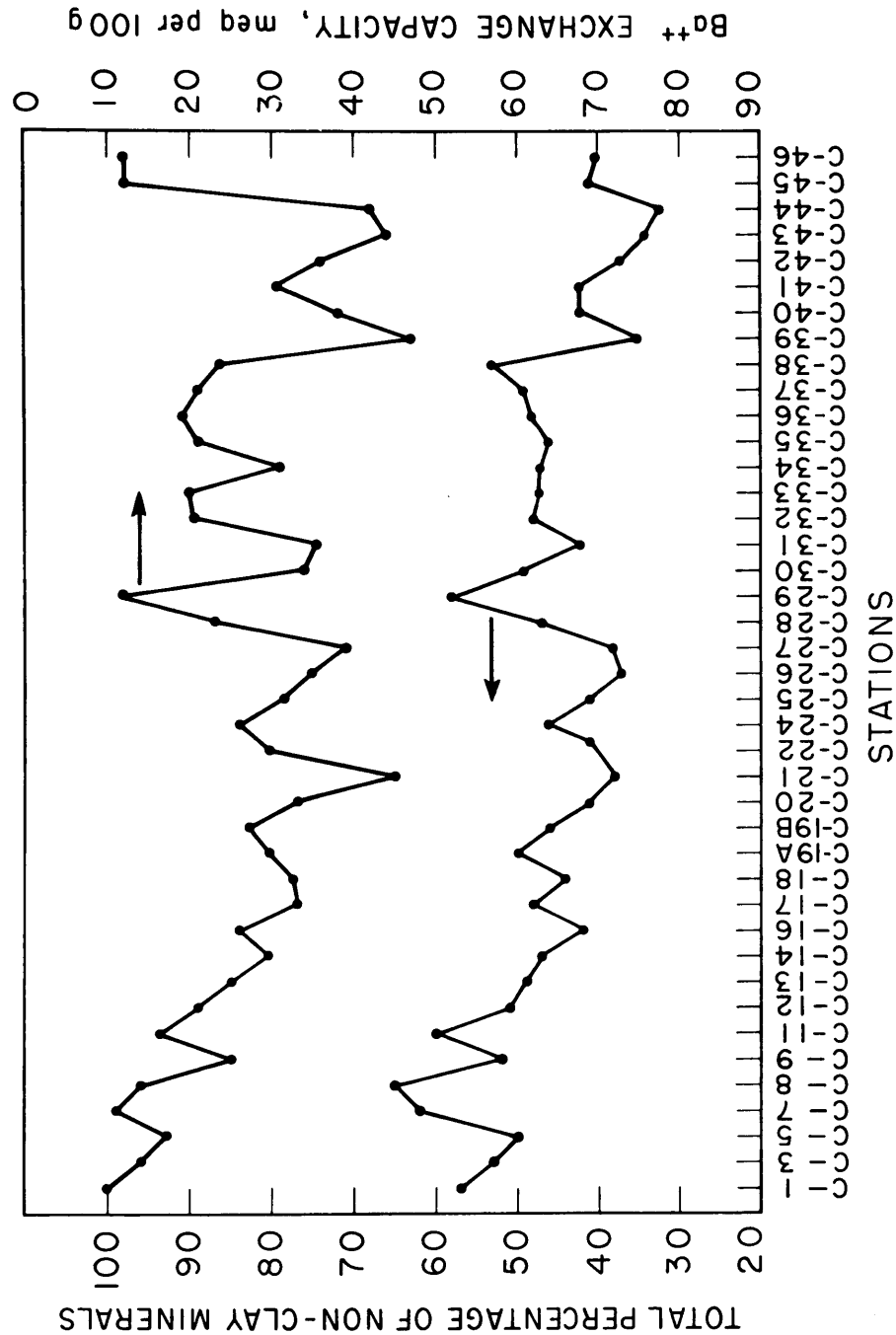


FIGURE 9. EXCHANGE CAPACITY

calculated values.

Using the values from Figure 9 in a ratio calculation, calculated exchange values can be obtained:

100-ncm:oev::cs:cev

where:

ncm = percent of non-clay minerals

cs = sample calculated as 100 percent clay

cev = calculated ion exchange value

oev = observed ion exchange value

The calculated exchange values (Fig. 10) range from 20 to 73 meq of barium per 100 grams for the heterogeneous clay characteristic of that particular sample. Considering the possible variations in the data used to obtain the calculated curve, no attempt should be made to use these data as precise values.

One other approach can be used to compare the exchange capacity of the fractionated sediment with the clay mineralogy. The top curve of Figure 10 indicates the relative amounts of clay present in the samples based on peak-area calculations for the composite 4.5 A spacing and for the 001 basal spacings of the various contributing clay minerals. The apparent lack of a clay contribution from the first ten samples can be attributed to presence of an amorphous phase that is significant volumetrically but which has so little crystallinity that there is no systematic reflection of the x-radiation.

The right two-thirds of the relative clay abundance curve reflects the trends shown by the exchange capacity curves and the non-clay

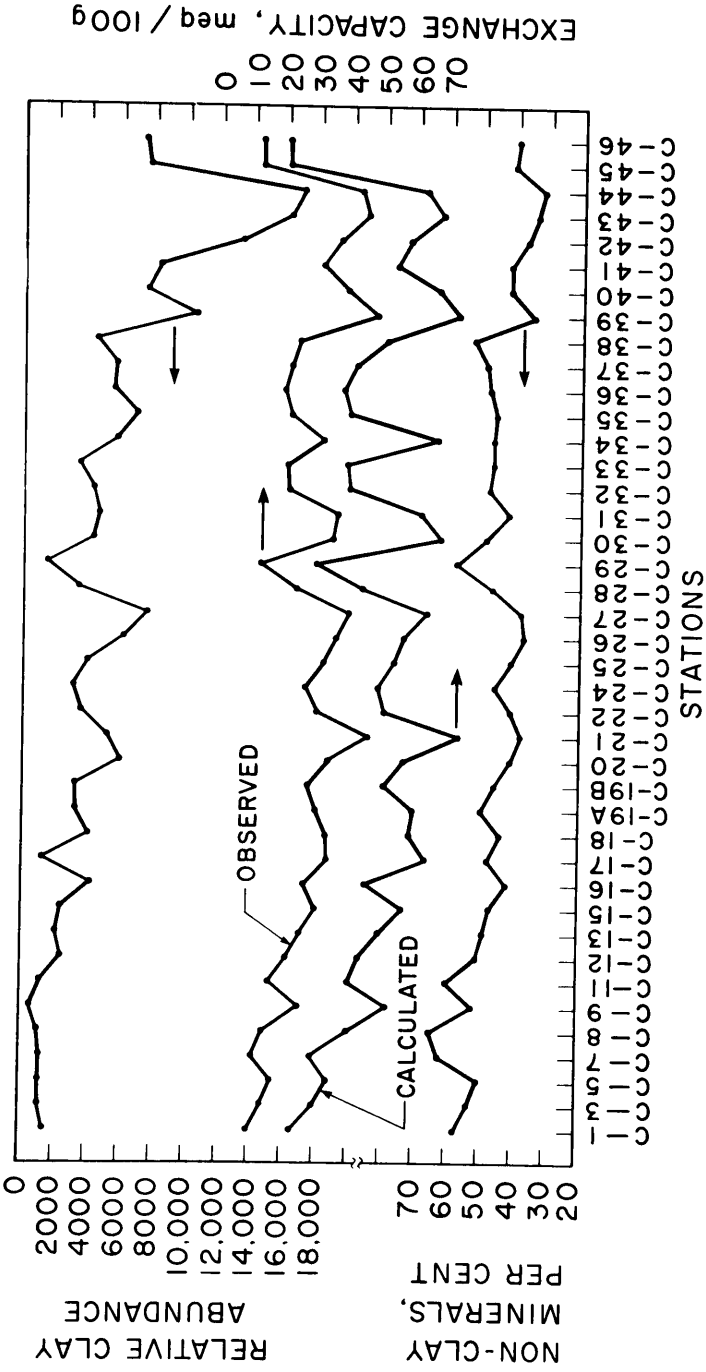


FIGURE 10. CALCULATED EXCHANGE CAPACITY VALUES

mineral percentage curve. The left one-third of the relative clay abundance curve, however, shows no such similarity. This perhaps shows best the almost complete loss of crystalline character of the degraded clays which make up the clay-sized sediments being transported in this portion of the Guadalupe River.

Radionuclide Sorption

The effectiveness of a clay for sorbing radioactive ions is usually expressed in terms of K_d, the distribution coefficient which is defined as:

$$K_d = \frac{fc/m}{fs/v}$$

where:

K_d = distribution coefficient
fc = fraction of activity sorbed by the clay in counts per minute
fs = fraction of activity left in the solution in counts per minute
m = weight of clay in grams
v = volume of master solution in milliliters.

Throughout these experiments the sediment-solution ratio for the radionuclide sorption studies was maintained at 500 mg/l. This then leaves two variables in the above equation that must be measured before the distribution constant (K_d) can be calculated. The two variables are: (1) the activity sorbed by the sediment and (2) the activity remaining in solution. The distribution constant (K_d), however, is unique within the limits of the particular experimental technique

because no consideration is given to the exchange capacity of the sediments or to the presence of competing ions in the solution.

The distribution coefficient then, represents an equilibrium value for a particular sediment-solution ratio and only for a given condition.

This study was concerned with two radionuclides, cesium-137 and strontium-89, and the associated problems of sorption and release of these radionuclides by the sediments of the Guadalupe River and San Antonio Bay. Because these sediments contained an organic fraction associated with the clays, some provision for evaluating the different constituents was required.

Accordingly, the fractionated sediments were divided into two groups; one group was treated to remove the organic constituents while the other group remained in its natural state. Both treated and untreated portions of the samples were processed through the laboratory procedure at the same time so that sample conditions and handling would be as similar as possible.

Figures 11 and 12 are tables of data obtained during the strontium-89 studies for the untreated sediments and for the samples that were treated to remove the organic constituents.

Strontium-89. The data from Figures 11 and 12 can be summarized as follows:

1. The highest rate of strontium-89 sorption occurred during the first hour of sediment-solution contact.

Figure 11 Strontium - 89 Sorption, Untreated Samples

Sample	Variable	Duration of Contact 1 Hour	1 Day	3 Days	7 Days
C-1	Sorption (%)	55.3	54.7	56.9	59.8
	K_d (ml/gm)	2480	2410	2640	2900
	pH	9.5	9.4	8.8	8.2
C-3	Sorption (%)	50.9	51.2	52.0	54.4
	K_d (ml/gm)	2070	2100	2170	2400
	pH	9.5	9.5	9.1	8.5
C-5	Sorption (%)	50.2	50.3	50.6	51.8
	K_d (ml/gm)	2010	2030	2050	2150
	pH	9.5	9.4	9.0	8.4
C-7	Sorption (%)	51.5	51.1	51.2	52.2
	K_d (ml/gm)	2130	2090	2100	2180
	pH	9.5	9.4	9.1	8.5
C-8	Sorption (%)	51.5	50.6	52.1	52.8
	K_d (ml/gm)	2120	2050	2180	2240
	pH	9.5	9.4	9.0	8.8
C-9	Sorption (%)	46.7	47.1	50.2	51.2
	K_d (ml/gm)	1750	1780	2020	2100
	pH	9.5	9.4	9.1	8.5
C-11	Sorption (%)	52.2	53.0	52.7	55.6
	K_d (ml/gm)	2180	2250	2230	2510
	pH	9.5	9.4	9.1	8.5
C-12	Sorption (%)	46.3	46.0	46.2	47.8
	K_d (ml/gm)	1720	1710	1720	1830
	pH	9.5	9.3	8.8	8.3
C-13	Sorption (%)	49.6	49.5	50.3	50.2
	K_d (ml/gm)	1970	1960	2030	2020
	pH	9.5	9.3	8.9	8.6
C-14	Sorption (%)	48.4	49.6	51.2	52.6
	K_d (ml/gm)	1880	1970	2100	2220
	pH	9.5	9.4	9.1	8.4
C-16	Sorption (%)	53.6	53.8	54.8	56.0
	K_d (ml/gm)	2310	2330	2420	2550
	pH	9.5	9.4	8.9	8.3

Figure 11 Strontium - 89 Sorption, Untreated Samples (cont'd)

Sample	Variable	Duration of Contact 1 Hour	1 Day	3 Days	7 Days
C-17	Sorption (%)	51.4	52.2	52.3	52.4
	K_d (ml/gm)	2120	2180	2190	2200
	pH	9.4	9.5	8.8	8.6
C-18	Sorption (%)	54.6	54.8	55.6	58.4
	K_d (ml/gm)	2400	2420	2510	2810
	pH	9.5	9.5	9.0	8.6
C-20	Sorption (%)	52.2	53.7	56.9	58.0
	K_d (ml/gm)	2180	2320	2640	2760
	pH	9.4	9.4	8.9	8.6
C-21	Sorption (%)	54.9	54.8	54.9	58.0
	K_d (ml/gm)	2440	2420	2430	2760
	pH	9.5	9.5	9.2	8.5
C-22	Sorption (%)	55.2	55.8	56.0	57.0
	K_d (ml/gm)	2460	2530	2550	2650
	pH	9.5	9.1	9.0	8.4
C-24	Sorption (%)	54.2	53.6	54.6	55.6
	K_d (ml/gm)	2370	2310	2410	2510
	pH	9.6	9.2	9.0	8.5
C-25	Sorption (%)	55.7	56.5	56.3	58.3
	K_d (ml/gm)	2510	2590	2570	2800
	pH	9.5	9.2	8.7	8.5
C-26	Sorption (%)	55.6	57.2	57.4	59.9
	K_d (ml/gm)	2510	2670	2700	3000
	pH	9.6	9.2	9.0	8.8
C-27	Sorption (%)	58.0	58.6	59.2	61.6
	K_d (ml/gm)	2760	2830	2900	3200
	pH	9.5	9.2	9.0	8.8
C-28	Sorption (%)	56.4	56.0	57.0	57.6
	K_d (ml/gm)	2590	2550	2650	2720
	pH	9.5	9.2	9.2	8.8
C-30	Sorption (%)	54.6	54.5	55.8	56.1
	K_d (ml/gm)	2410	2390	2530	2560
	pH	9.5	9.4	9.3	8.8

Figure 11 Strontium - 89 Sorption, Untreated Samples (cont'd)

Sample	Variable	Duration of Contact 1 Hour	1 Day	3 Days	7 Days
C-31	Sorption (%)	55.9	56.0	56.6	57.3
	K_d (ml/gm)	2530	2550	2610	2680
	pH	9.6	9.4	9.3	8.9
C-34	Sorption (%)	50.8	51.2	51.4	52.8
	K_d (ml/gm)	2070	2100	2120	2240
	pH	9.6	9.4	9.1	8.8
C-39	Sorption (%)	54.7	54.8	55.4	56.7
	K_d (ml/gm)	2410	2430	2480	2610
	pH	9.6	9.2	9.2	8.8

Figure 12 Strontium - 89 Sorption, Organic Material Removed

Sample	Variable	Duration of Contact 1 Hour	1 Day	3 Days	7 Days
C-1	Sorption (%)	42.5	42.5	43.3	44.1
	K_d (ml/gm)	1480	1480	1530	1580
	pH	9.5	9.5	9.1	8.5
C-3	Sorption (%)	42.8	44.3	44.6	47.6
	K_d (ml/gm)	1500	1590	1610	1820
	pH	9.5	9.5	9.1	8.7
C-5	Sorption (%)	43.0	44.3	45.1	47.8
	K_d (ml/gm)	1510	1590	1650	1830
	pH	9.5	9.6	9.2	8.6
C-7	Sorption (%)	36.5	37.3	38.4	41.7
	K_d (ml/gm)	1150	1190	1250	1430
	pH	9.5	9.5	9.3	8.6
C-8	Sorption (%)	36.9	38.2	41.9	45.4
	K_d (ml/gm)	1170	1240	1440	1660
	pH	9.5	9.5	9.4	8.8
C-9	Sorption (%)	34.0	33.9	34.6	36.1
	K_d (ml/gm)	1050	1020	1060	1130
	pH	9.7	9.6	9.5	8.8
C-11	Sorption (%)	38.0	38.4	37.3	38.7
	K_d (ml/gm)	1230	1250	1190	1270
	pH	9.6	9.5	9.3	8.7
C-12	Sorption (%)	45.2	45.9	47.9	49.3
	K_d (ml/gm)	1650	1690	1840	1950
	pH	9.5	9.5	9.3	8.6
C-13	Sorption (%)	44.1	44.5	44.4	45.2
	K_d (ml/gm)	1580	1610	1600	1650
	pH	9.5	9.5	9.3	8.6
C-14	Sorption (%)	41.9	42.8	43.9	45.2
	K_d (ml/gm)	1440	1500	1540	1650
	pH	9.6	9.6	9.4	8.7
C-16	Sorption (%)	46.6	46.3	46.4	46.9
	K_d (ml/gm)	1750	1720	1730	1770
	pH	9.5	9.6	9.3	8.9
C-17	Sorption (%)	29.8	32.1	37.2	46.5
	K_d (ml/gm)	850	950	1190	1740
	pH	9.6	9.7	9.5	8.8
C-18	Sorption (%)	46.5	46.9	49.5	50.2
	K_d (ml/gm)	1740	1770	1960	2020
	pH	9.6	9.6	9.4	8.9

Figure 12 Strontium - 89 Sorption, Organic Material Removed (Cont'd)

Sample	Variable	Duration of Contact 1 Hour	1 Day	3 Days	7 Days
	Sorption (%)	43.0	44.1	49.1	54.1
C-20	K_d (ml/gm)	1510	1580	1930	2360
	pH	9.6	9.6	9.4	8.7
	Sorption (%)	48.1	48.8	50.3	51.5
C-21	K_d (ml/gm)	1860	1910	2030	2130
	pH	9.5	9.5	9.4	8.7
	Sorption (%)	44.2	45.7	46.3	47.4
C-22	K_d (ml/gm)	1580	1680	1720	1800
	pH	9.6	9.2	9.2	9.2
	Sorption (%)	41.6	42.1	43.0	43.3
C-24	K_d (ml/gm)	1430	1460	1510	1530
	pH	9.6	9.4	9.5	9.4
	Sorption (%)	43.3	43.9	44.7	48.3
C-25	K_d (ml/gm)	1530	1570	1620	1870
	pH	9.5	9.2	8.7	8.5
	Sorption (%)	46.7	47.1	47.9	48.7
C-26	K_d (ml/gm)	1750	1780	1840	1900
	pH	9.6	9.2	9.0	8.8
	Sorption (%)	47.9	48.2	49.0	49.6
C-27	K_d (ml/gm)	1840	1860	1920	1970
	pH	9.4	9.2	9.0	8.8
	Sorption (%)	39.6	40.0	40.8	41.4
C-28	K_d (ml/gm)	1310	1330	1380	1410
	pH	9.5	9.4	9.3	8.8
	Sorption (%)	42.7	43.5	44.8	45.5
C-30	K_d (ml/gm)	1490	1540	1620	1670
	pH	9.6	9.2	9.3	9.1
	Sorption (%)	39.3	39.7	40.7	42.8
C-31	K_d (ml/gm)	1290	1320	1380	1500
	pH	9.5	9.2	9.4	9.1
	Sorption (%)	41.7	41.8	42.2	42.6
C-34	K_d (ml/gm)	1430	1440	1460	1480
	pH	9.7	9.5	9.2	9.3
	Sorption (%)	46.2	46.5	46.9	47.9
C-39	K_d (ml/gm)	1720	1740	1770	1840
	pH	9.6	9.4	9.3	9.4

2. The amount of strontium-89 sorbed by the sediments slowly increased with time.
3. The pH of the solution decreased with increasing time.
4. The untreated samples had a higher initial and final sorption percentage and K_d values than did the samples in which the organic constituent had been removed.

Cesium-137. Figures 13 and 14 are tables of data obtained during the cesium-137 studies of the radionuclide sorption on both untreated and treated samples.

A summary of these data is as follows:

1. The highest rate of cesium-137 sorption occurred during the first hour of sediment-solution contact.
2. The amount of cesium-137 sorbed by the sediments slowly increased with time.
3. The pH of the solution decreased with increasing time.
4. The untreated samples had a higher initial and final sorption percentage and K_d values than did the samples in which the organic constituents had been removed.

Radionuclide Release

The previous section discussed strontium-89 and cesium-137 sorption studies made with carrier-free radionuclides in distilled water. This laboratory approach by necessity uses many simplifications that are hard to reconcile with the harsh requirements posed by practical problems.

Figure 13 Cesium - 137 Sorption, Untreated Samples

Sample	Variable	Duration of Contact 1 Hour	1 Day	3 Days	7 Days
C-1	Sorption (%)	94.5	94.6	95.0	95.7
	K_d (ml/gm)	34,600	35,000	38,000	44,500
	pH	9.4	9.3	8.7	8.9
C-3	Sorption (%)	89.4	90.8	91.6	92.4
	K_d (ml/gm)	16,900	19,900	21,800	24,400
	pH	9.5	9.4	9.2	8.8
C-5	Sorption (%)	91.1	91.4	91.5	92.2
	K_d (ml/gm)	20,600	21,200	21,700	23,600
	pH	9.5	9.2	9.0	8.9
C-7	Sorption (%)	90.2	90.3	91.1	92.2
	K_d (ml/gm)	18,400	18,400	20,500	23,600
	pH	9.5	9.5	9.2	9.1
C-8	Sorption (%)	90.8	91.0	91.3	91.9
	K_d (ml/gm)	19,700	20,200	21,000	22,600
	pH	9.5	9.5	9.2	8.9
C-9	Sorption (%)	90.7	90.9	91.2	91.3
	K_d (ml/gm)	19,300	20,100	20,600	21,000
	pH	9.6	9.6	9.3	9.0
C-11	Sorption (%)	91.2	91.2	91.1	91.3
	K_d (ml/gm)	20,600	20,600	20,500	21,000
	pH	9.6	9.6	9.3	9.0
C-12	Sorption (%)	91.5	91.4	91.6	91.8
	K_d (ml/gm)	21,700	21,200	21,900	22,500
	pH	9.6	9.5	9.3	8.9
C-13	Sorption (%)	91.5	91.6	92.1	92.9
	K_d (ml/gm)	21,700	21,900	23,200	26,100
	pH	9.5	9.5	9.3	9.0
C-14	Sorption (%)	91.2	91.3	91.7	92.4
	K_d (ml/gm)	20,600	21,000	22,000	24,400
	pH	9.5	9.5	9.3	9.1
C-16	Sorption (%)	93.0	93.2	93.4	93.6
	K_d (ml/gm)	26,600	27,500	28,300	29,300
	pH	9.6	9.5	9.2	9.0
C-17	Sorption (%)	91.2	91.4	91.6	92.2
	K_d (ml/gm)	20,600	21,200	21,900	23,600
	pH	9.5	9.5	9.2	8.8
C-18	Sorption (%)	92.2	92.1	92.4	92.3
	K_d (ml/gm)	23,600	23,200	24,400	24,100
	pH	9.5	9.6	9.1	8.9

Figure 13 Cesium - 137 Sorption, Untreated Samples (Cont'd)

Sample	Variable	Duration of Contact 1 Hour	1 Day	3 Days	7 Days
C-20	Sorption (%)	91.9	92.1	92.2	92.3
	K_d (ml/gm)	22,600	23,200	23,600	24,100
	pH	9.5	9.1	8.3	8.3
C-21	Sorption (%)	92.5	92.8	93.4	93.7
	K_d (ml/gm)	24,800	25,900	28,300	29,700
	pH	9.5	9.4	8.4	8.1
C-22	Sorption (%)	91.6	91.8	92.2	92.8
	K_d (ml/gm)	21,900	22,500	23,600	25,900
	pH	9.4	9.3	8.9	8.5
C-24	Sorption (%)	91.2	91.4	92.2	94.1
	K_d (ml/gm)	20,600	21,200	23,600	32,000
	pH	9.6	9.6	9.2	8.7
C-25	Sorption (%)	93.0	93.1	93.6	94.6
	K_d (ml/gm)	26,600	27,100	29,300	35,000
	pH	9.6	9.5	9.1	8.8
C-26	Sorption (%)	93.2	93.4	93.9	94.1
	K_d (ml/gm)	27,500	28,300	30,800	32,000
	pH	9.6	9.5	9.2	8.8
C-27	Sorption (%)	93.0	93.1	94.5	94.7
	K_d (ml/gm)	26,600	27,100	34,600	35,700
	pH	9.6	9.5	9.2	8.8
C-28	Sorption (%)	90.5	90.9	92.2	93.3
	K_d (ml/gm)	19,100	20,200	23,600	27,800
	pH	9.5	9.6	9.3	9.0
C-29	Sorption (%)	90.6	91.0	92.1	92.4
	K_d (ml/gm)	19,200	20,200	23,200	24,400
	pH	9.5	9.5	8.5	8.5
C-30	Sorption (%)	91.7	92.0	92.3	92.8
	K_d (ml/gm)	22,300	23,000	24,100	25,900
	pH	9.5	9.4	9.1	8.6
C-31	Sorption (%)	91.0	91.2	91.6	92.1
	K_d (ml/gm)	20,200	20,600	21,900	23,200
	pH	9.6	9.6	9.2	8.1
C-34	Sorption (%)	89.7	90.0	90.8	91.2
	K_d (ml/gm)	17,400	18,000	19,700	20,600
	pH	9.6	9.5	8.8	8.8

Figure 13 Cesium - 137 Sorption, Untreated Samples (Cont'd)

Sample	Variable	Duration of Contact 1 Hour	1 Day	3 Days	7 Days
C-36	Sorption (%)	90.8	91.2	91.3	91.9
	K_d (ml/gm)	19,700	20,600	21,000	22,600
	pH	9.6	9.6	9.0	9.0
C-39	Sorption (%)	89.8	90.2	90.8	91.6
	K_d (ml/gm)	17,500	18,400	19,700	21,900
	pH	9.5	9.5	8.5	8.5
C-42	Sorption (%)	90.7	90.8	91.2	91.3
	K_d (ml/gm)	19,600	19,700	20,600	21,000
	pH	9.7	9.7	9.2	9.1
C-45	Sorption (%)	91.6	91.8	92.1	92.3
	K_d (ml/gm)	21,900	22,500	23,200	24,100
	pH	9.5	9.6	9.2	8.9
C-46	Sorption (%)	90.9	90.9	91.7	92.1
	K_d (ml/gm)	20,200	20,200	22,300	23,200
	pH	9.5	9.6	9.4	9.0

Figure 14 Cesium - 137 Sorption, Organic Material Removed

Sample	Variable	Duration of Contact 1 Hour	1 Day	3 Days	7 Days
C-1	Sorption (%)	88.2	88.3	89.1	89.8
	K_d (ml/gm)	14,900	15,100	16,400	17,600
	pH	9.5	9.5	9.1	8.6
C-3	Sorption (%)	86.8	87.1	87.6	89.0
	K_d (ml/gm)	13,100	13,500	14,100	16,200
	pH	9.7	9.6	9.4	9.2
C-5	Sorption (%)	86.2	86.7	87.6	89.2
	K_d (ml/gm)	12,500	13,000	14,100	16,500
	pH	9.6	9.5	9.5	9.2
C-7	Sorption (%)	87.3	87.7	88.8	89.7
	K_d (ml/gm)	13,700	14,300	15,900	17,500
	pH	9.5	9.6	9.5	9.0
C-8	Sorption (%)	87.2	87.7	88.0	88.9
	K_d (ml/gm)	13,600	14,300	14,700	16,100
	pH	9.6	9.6	9.4	8.3
C-9	Sorption (%)	87.2	87.5	87.9	87.8
	K_d (ml/gm)	13,600	14,000	14,500	14,400
	pH	9.6	9.6	9.4	9.1
C-11	Sorption (%)	84.8	85.0	86.3	87.4
	K_d (ml/gm)	11,100	11,300	12,600	13,900
	pH	9.6	9.6	9.3	9.0
C-12	Sorption (%)	85.0	85.2	85.8	85.9
	K_d (ml/gm)	11,300	11,600	12,100	12,200
	pH	9.7	9.6	9.4	8.3
C-13	Sorption (%)	88.9	89.0	89.6	89.9
	K_d (ml/gm)	16,100	16,200	17,200	17,700
	pH	9.6	9.6	9.2	8.8
C-14	Sorption (%)	87.9	88.1	88.3	88.4
	K_d (ml/gm)	14,500	14,900	15,100	15,200
	pH	9.6	9.6	9.4	9.2
C-16	Sorption (%)	85.5	86.1	87.6	88.4
	K_d (ml/gm)	11,800	12,400	14,100	15,200
	pH	9.6	9.6	9.5	9.4

Figure 14- Cesium - 137 Sorption, Organic Material Removed (Cont'd)

Sample	Variable	Duration of Contact 1 Hour	1 Day	3 Days	7 Days
C-17	Sorption (%)	87.9	88.2	89.4	90.8
	K_d (ml/gm)	14,600	14,900	16,800	19,900
	pH	9.7	9.6	9.4	9.2
C-18	Sorption (%)	88.6	88.8	89.0	89.1
	K_d (ml/gm)	15,500	15,900	16,200	16,400
	pH	9.7	9.6	9.4	9.2
C-20	Sorption (%)	90.5	90.6	91.0	91.5
	K_d (ml/gm)	19,100	19,400	20,200	21,600
	pH	9.6	9.6	9.4	9.0
C-21	Sorption (%)	91.7	91.7	92.2	92.4
	K_d (ml/gm)	22,200	22,700	23,800	24,400
	pH	9.6	9.6	9.4	9.0
C-22	Sorption (%)	90.6	90.8	91.0	91.1
	K_d (ml/gm)	19,300	19,700	20,200	20,600
	pH	9.4	9.6	9.3	9.0
C-24	Sorption (%)	89.3	89.5	90.4	90.8
	K_d (ml/gm)	16,700	17,100	18,800	19,700
	pH	9.7	9.6	9.5	9.2
C-25	Sorption (%)	88.7	89.0	90.4	91.0
	K_d (ml/gm)	15,700	16,200	19,000	20,200
	pH	9.6	9.6	9.5	9.2
C-26	Sorption (%)	88.8	89.0	89.1	89.4
	K_d (ml/gm)	15,900	16,200	16,400	16,800
	pH	9.5	9.7	9.4	9.1
C-27	Sorption (%)	87.4	87.9	88.6	89.5
	K_d (ml/gm)	13,900	14,600	15,600	17,000
	pH	9.6	9.6	9.3	8.7
C-28	Sorption (%)	90.3	90.4	90.8	90.9
	K_d (ml/gm)	18,700	19,000	19,900	20,100
	pH	9.6	9.6	9.3	8.7
C-29	Sorption (%)	88.0	88.2	88.4	88.5
	K_d (ml/gm)	14,700	15,000	15,200	15,400
	pH	9.6	9.6	9.3	8.9

Figure 14- Cesium - 137 Sorption, Organic Material Removed (Cont'd)

Sample	Variable	Duration of Contact 1 Hour	1 Day	3 Days	7 Days
C-30	Sorption (%)	89.7	89.8	90.7	91.5
	K_d (ml/gm)	17,400	17,400	19,500	21,500
	pH	9.7	9.6	9.1	8.8
C-31	Sorption (%)	88.6	88.8	90.4	91.6
	K_d (ml/gm)	15,600	15,900	19,000	21,900
	pH	9.5	9.6	9.3	8.9
C-34	Sorption (%)	86.8	87.3	89.0	90.1
	K_d (ml/gm)	13,200	13,700	16,200	18,200
	pH	9.6	9.6	9.4	9.0
C-36	Sorption (%)	89.0	89.4	90.2	91.5
	K_d (ml/gm)	16,200	16,800	18,400	21,500
	pH	9.6	9.6	9.3	8.9
C-39	Sorption (%)	89.0	89.3	89.6	89.9
	K_d (ml/gm)	16,200	16,700	17,200	17,800
	pH	9.5	9.6	9.3	8.9
C-42	Sorption (%)	88.5	88.8	89.1	89.8
	K_d (ml/gm)	15,400	15,900	16,400	17,600
	pH	9.5	9.6	9.3	8.9
C-45	Sorption (%)	88.3	89.0	89.4	91.6
	K_d (ml/gm)	15,100	16,200	16,800	21,900
	pH	9.5	9.4	9.3	8.9
C-46	Sorption (%)	88.0	88.9	89.6	91.7
	K_d (ml/gm)	14,700	16,100	17,200	22,200
	pH	9.5	9.4	9.3	8.9

In order that the sorption studies could have a more direct application it was decided to place one of the radioactive samples in water samples collected from the Guadalupe River and San Antonio Bay and record the release of radionuclides that would occur in those environments.

These experiments followed the previously detailed laboratory procedures with the exception that water from the Guadalupe River and not distilled water was used as the solution. At the end of these sorption studies, the samples were centrifuged to separate water and sediment, the supernatant liquid was decanted, and an equal amount of bay water was added. These samples again followed the laboratory process described above.

Figures 15 and 16 indicate the amount of cesium-137 and strontium-89, respectively, that would be sorbed in the fluvial environment and later be released when the sediment was transported into the bay environment. A comparison of these data with the laboratory studies using distilled water suggests several interesting results:

1. There is virtually no difference in the sorption of cesium-137 under the two diverse conditions.
2. The sorption of strontium-89 is sensitive to the fluvial environment; sorption decreases from approximately 50 percent to 10 percent.
3. When the sediments were transported into the bay environment, approximately 42 percent of the sorbed cesium-137 and strontium-89 would be released.

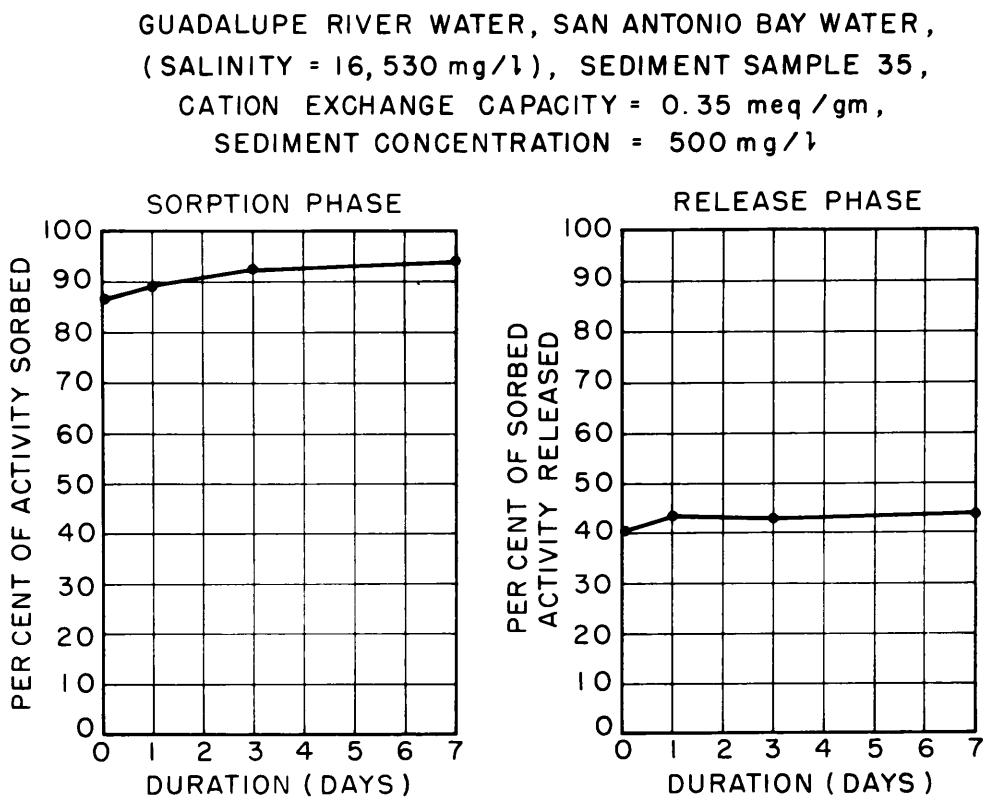


FIGURE 15. SORPTION OF Cs^{137} IN FRESH WATER AND ITS RELEASE IN SALT WATER.

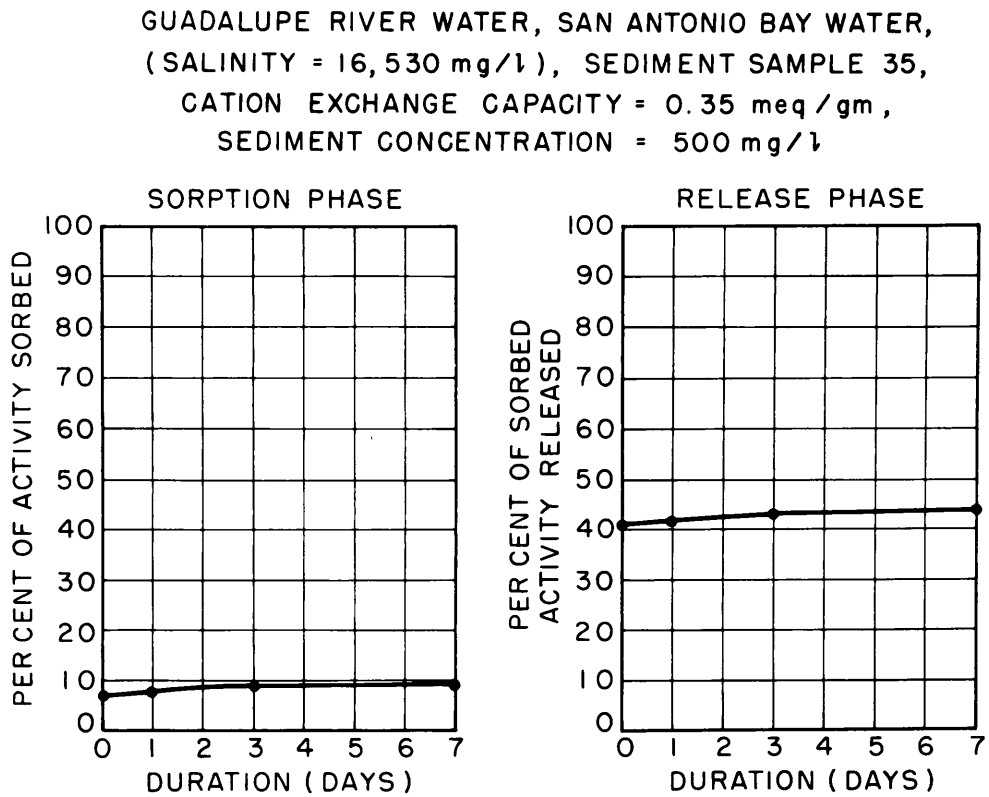


FIGURE 16. SORPTION OF Sr^{89} IN FRESH WATER AND ITS RELEASE IN SALT WATER.

4. The rate of exchange, both sorption and release, is extremely high during the first hour of contact.

DISCUSSION

Clay Minerals

The clay minerals in the Recent sediments of the Guadalupe River and San Antonio Bay are interpreted as crystalline remnants of the weathered and degraded parent lithology. The clay sediment can be best described as a heterogeneous clay mineral complex with some expandable layers within the crystallines. X-ray diffraction patterns are not characteristic of a single clay mineral but rather reflect the degraded and composite character of the sediment. The clay reflections are low in intensity and diffuse. Some of the minor features can be attributed to a single clay mineral but these reflections are also broad and diffuse in contrast to the sharp narrow reflections which are characteristic of a well crystallized material.

The asymmetry of the basal reflection and the generally broad character of the other reflections suggest that this debris should be considered as a heterogeneous mixed-layer clay-mineral complex of poor crystallinity.

Many investigators (Bradley, 1954; Grim and Johns, 1954; Murray and Sayyab, 1955; Weaver, 1953) have observed that the mass of sediments currently being discharged by streams into the oceans is transported in an ion-deficient condition. Such material is difficult to describe and compare with the more crystalline clay minerals. Much of this degraded micaceous material has been variously described as possessing montmorillonite-like, illite-like, or chlorite-like characteristics; but the properties generally considered to be diagnostic

for the more crystalline varieties can seldom be adopted without modification to classify the degraded varieties.

Grim and Johns (1954, p. 85) enumerated some of the difficulties associated with the analysis of complex clay mineral mixtures occurring in sediments of the Northern Gulf of Mexico. The major problem is the interpretation of the x-ray diffraction data and the nomenclature of the poorly crystalline clay minerals.

The heating test suggested by Brindley (1951, p. 49) for distinguishing between chlorite and kaolinite does not appear to be applicable to poorly crystalline materials. Murray and Sayyab (1955, p. 435) commented that heating to 525-550°C destroyed the basal reflections of both kaolinite and chlorite in the Recent sediment cores that they investigated. Grim and Johns (1954, p. 87) have also commented on the need for modifying the heating technique for the identification of minerals in Recent sediments. Nelson (1960, p. 141) concluded that in Recent sediments both chlorite and kaolinite undergo thermal breakdown at the same temperature and that the classic heat treatment is not valid.

The Guadalupe River sediments were characterized by Grim and Johns (1954, p. 94) as containing a dominance of montmorillonite with insignificant amounts of illite and a third component indicated as chlorite. A commensurate increase in the illite and chlorite phases as montmorillonite decreased was noted in the marine environment.

Grim and Johns (1954, p. 85, 86) concluded that the bulk of the argillaceous materials in the sediments of San Antonio Bay were

three-layer silicates, montmorillonite, illite and chlorite. They recognized two distinct types of montmorillonite: a 15.5 A two-layer hydrate chracterized by calcium ions in the exchange position and a second type that exhibited properties common to both montmorillonite and chlorite.

This second type of montmorillonite was explained (Grim and Johns, 1954, p. 87) as having an interlayer region consisting of occasional "islands" of brucite scattered randomly over the otherwise hydrated montmorillonite surfaces. These brucite "islands" were considered to occur with sufficient frequency to prevent a complete collapse of the structure with moderate heating yet were too few to prevent glycolation and subsequent expansion. This material could represent either incipient chloritization of the montmorillonite structure or be the skeletal structure of a chlorite degraded by the removal of magnesium.

It is difficult to reconcile the observations of Grim and Johns (1954) with the studies by Simons and Taggart (1954) regarding the clay mineral content of Gulf Coast formations that crop out in the Guadalupe River Basin. Simons and Taggart (1954, p. 107), using both x-ray and electron microscope techniques, observed that montmorillonite, kaolinite and illite were the predominant clay minerals; no trace of chlorite or vermiculite was recorded.

Kunze, et al. (1955, p. 383) in their studies of Texas soils concluded that clay mineral development within the soil profile was negligible and that the weathering processes modified the mineral

composition of the soil with relative rapidity. Studies of cores indicated that the surface material was of poorer crystallinity than material from deeper horizons. The decomposition of both kaolinite and montmorillonite was observed in the surface horizons of several of the profiles studied.

Weaver (1958) concluded from an exhaustive study that clays are primarily detrital in origin rather than of an environmental diagenetic origin. He suggested that the source material and type of weathering was the major factor in determining the type of clay found in a given environment.

An important point in the discussion of diagenesis vs. detrital origin is the definition and usage of the term "diagenesis." The concept is real but the interpretation and usage of the term are extremely subjective among the various workers in the field, which is part of the problem.

The Recent sediments of the Guadalupe River and San Antonio Bay cannot be interpreted by using many of the classic identification techniques such as heating and glycolation. This heterogeneous and degraded material does not respond in the same manner as the more crystalline varieties. Some subjective interpretation is required by the investigator in order to decide to what extent the common classification criteria should be extended.

The use of the same nomenclature to describe both the well crystallized varieties and the degraded material, which cannot meet the usual classification parameters, presents an incomplete and

and erroneous view. The important point is the degraded nature of this material and the diverse properties of expansion and collapse that it possesses. This unusual combination of properties seems sufficiently unique to warrant mention in the nomenclature.

Exchange Capacity

Ion exchange can be defined as the exchange of an ion held by an electrical charge near the surface of an exchange mineral with an ion present in a solution in which the exchange mineral is immersed (Robinson, 1962, p. 60). Ion exchange reactions are stoichiometric and follow the law of mass action (Grim, 1953, p. 136).

Grim (1953, p. 132-134) lists three causes of ion exchange in minerals:

1. Broken bonds along the edges of the particle.
2. Ion substitutions within the crystal lattice.
3. Replacement of the hydrogen of exposed hydroxyls by cations.

Because of the difficulty of distinguishing between absorption (the penetration of a solute into a sorbent) and adsorption (the uptake of a solute on the surface of a sorbent), the inclusive term sorption is generally used (Maron and Prunton, 1958, p. 214).

It is important to remember that in ion exchange and sorption reactions a dissolved ion is taken up by a solid. The basic difference in the two processes is the method of ion acquisition. The ion-exchange reaction is stoichiometric; every ion exchanged must be replaced by an equivalent amount of another ion or ions. In the sorption reaction, an ion can be taken up without any subsequent

release (Helfferich, 1962, p. 6). Ideally the two processes are distinct, but in reality the two reactions occur together.

An excellent literature review of ion exchange by clays and other minerals is presented by Carroll (1959). Robinson (1962) presented an extensive literature survey of ion exchange minerals and the problems associated with the disposal of radioactive waste. Helfferich (1962) considers not only the theoretical approach and experimental techniques but also includes a discussion of the various ion-exchange operations used in industry.

Intuitively one might assume that a clay with a high ion exchange capacity would be more effective in removing radionuclides from solutions than a clay with a low ion exchange capacity, but this assumption is not supported by data available in the literature. The exchange capacity of a clay seems to give little or no indication as to the ability of the clay to remove tracer level quantities of radionuclides from solution (Brockett and Placak, 1953, p. 12).

Studies by Jacobs and Tamura (1960, p. 211), Tamura and Jacobs (1960, p. 150), and Struxness, et al. (1960, p. 60) suggest that structure selectivity is of more importance in cesium sorption than is ion exchange capacity. Sodium montmorillonite heated to 700°C showed a sharp decrease in exchange capacity as the structure was modified and collapsed. Yet this same collapsed montmorillonite had the highest cesium sorption observed, provided sufficient contact time was allowed.

The natural material gave sorption curves that could be described

by a single equilibrium coefficient. When the expanded clay structure had been collapsed by treatment to 10 A, the material had improved capacity for cesium sorption (Tamura and Jacobs, 1960b, p. 395). The sorption curves, however, did not show the simple exchange that some investigators have envisioned.

The concept of multiple exchange sites has been proposed by many investigators: Marshall and Krimbill (1942), Marshall and Bergman (1942), Grim (1953, p. 133), Byrne (1954), Garrels and Christ (1956), Blackmon (1958), McAtee (1958), Struxness et al. (1960), Jacobs and Tamura (1960b), and Brown (1963). The multiple sites include the internal interlayer sites, external surfaces, and the edges of the crystallite.

Brown (1963, p. 82), adding to the work of Krishnamoorthy and Overstreet (1950), determined the order of replacing ability to be

$$Cs>Pb>Ba>Sr>Ca>Mg>Cu>Rb>K>NH_4>Ag>Na>Li$$

This exchange sequence shows several important trends (Brown, 1963, p. 83):

1. Divalent ions are adsorbed preferentially over monovalent ions with the exception of cesium.
2. The replacing ability for both monovalent and divalent ions increases as ionic radius increases (exception is copper).
3. Valence and not ionic radius appears to determine the replacement sequence. The notable exception is cesium.

In this report the term sorption is used to indicate both ion exchange and "sorption." However, because of the strong bonding

that is observed in some of the radionuclide-sediment reactions and the often unique reaction of the radionuclides in tracer level quantities, the term sorption is always used when discussing radionuclide reactions. Ion exchange or exchange capacity is used in this report following the customary terminology, but considering the material involved it is evident that both sorption and ion exchange are operative.

Exchange capacity determinations on the fractionated sediments of the Guadalupe River and San Antonio Bay showed variations ranging from 11 meq to 43 meq of barium per 100 grams of sediment. Because the non-clay mineral content of these sediments ranged from 32 to 65 percent, some variation in exchange capacity for the bulk sample was expected. A recalculation of the exchange capacity to remove the effect of the non-clay minerals increased the bulk exchange capacity to the range of 20 meq to 73 meq of barium per 100 grams of clay sediment.

Peak area calculations of the composite 4.5 A reflection and the basal (001) reflections of the various contributing clay species provide supporting data as to the quantity of clay present in relation to the exchange capacity. The discrete but poorly crystalline clay minerals such as kaolinite and illite that are present in some samples would also modify the exchange capacity determinations. However, because of the extensively degraded character of the heterogeneous clay mineral complex a precise identification of much of the clay contribution could not be made. The presence of a considerable

amount, perhaps as high as 30 percent, of amorphous material is indicated in the samples collected in the headwaters of the Guadalupe River.

The existence of an amorphous sediment fraction in soils is well documented in the literature. The literature review and research by Mitchell and Farmer (1962) documents occurrences in the United States, Japan, and New Zealand. The articles by Bates (1962) and Patterson (1964) discuss the occurrences of an amorphous material in the soil zones of Hawaii. Patterson (1964, p. 171) suggests that the amorphous materials may be either an intermediate stage between the destruction of the silicate minerals and the formation of clay minerals or that the amorphous fraction may form during the desilication of the clay minerals.

The amorphous material from the soils studied by Mitchell and Farmer (1962) could not be detected by x-radiation but could be detected by Differential Thermal Analysis and Infrared techniques. Because of compositional differences, primarily a higher silica content than normally reported for allophane, these authors apply the term hydrated amorphous aluminosilicates to describe that fraction which has an amorphous structure.

Although most sediment transported by stream systems is crystalline, only recently have investigators begun to realize that fine grained sediments may contain an appreciable quantity of amorphous inorganic material.

Although no attempt was made to determine the percentage of

organic material present in the various samples, a definite change in color was noticed as the organic material was oxidized with sodium hypochlorite. Story and Gloyna (1963, p. 75) report that the organic material present in the sediments of the San Marcos River, a tributary of the Guadalupe River, had an exchange capacity equal to 40 meq/100 g. The technique used for organic determination indicated that the organic fraction made up approximately 25 percent of the weight of the dry sample, a value that seems high for most sediments. Swain (1963, p. 104) reports that the quantity of humus in soils ranges from 0.5 to 10 percent. The predominant organic materials can be listed under the general headings of lignins, and their derivatives, proteins, hemicelluloses, lipoids, and other substances. Swain (1963, p. 119-120) lists almost two pages of specific organic substances that have been isolated from lake and ocean sediments.

Grim (1953, p. 132) reports that naturally occurring organic materials with high exchange capacities are restricted to recent sediments and soils; cation exchange values ranging from 150 to 500 meq/100 g. have been reported for the organic fraction present in some soils.

Radionuclide Sorption

The use of natural materials as a sorption medium is predicated on the ability of a mineral to sorb and retain a radionuclide. The disposal of the contaminated solid without additional treatment presents advantages in safety and economy of operation (Cowser, 1961, p. 40). Many micaceous materials are quite effective in removing

certain radionuclides from contaminated water (Robinson, 1962, Struxness et al., 1960, Cowser, 1961).

Struxness et al. (1960, p. 38) have shown that many sediments are effective in the decontamination of liquid-waste effluents. The decontamination process, however, results in contaminated sediments; these sediments may be subsequently leached as environmental conditions change or as the contaminated sediments are transported into another environment.

Seedhouse (1957, p. 415) lists the basic requirements for an exchange material to be used in an effluent system for the removal of radionuclides as:

1. Good permeability extending over a wide range of pH.
2. Stable particles that do not break down to collodial dimensions during treatment.
3. High exchange capacity.
4. Rapid rate of exchange.
5. Low cost.

Although the requirements listed above are used to evaluate materials for exchange column studies, many of these same requirements are equally applicable to the natural environment.

The most direct measure of the decontamination effectiveness of a mineral is the K_d value. K_d is usually defined as the ratio of radionuclide sorbed per gram of mineral to the radionuclide remaining unsorbed per milliliter of solution.

The value of the distribution constant (K_d) is dependent on the

concentration and chemical properties of the other ions present in the water. Struxness et al. (1960, p. 87) reported that experimental K_d values are time-dependent and have been observed to increase even after six months of contact time. Organic constituents present in the sediment may also play an important role in radionuclide sorption (Struxness et al., 1960, p. 57).

Sorathesn et al. (1960, p. 22) observed that when considering tracer level sorption by clays, the ion exchange capacity of the clay is not as important as their structural properties. The amount of tracer radionuclide sorbed by illite and vermiculite increased with increasing contact time. Montmorillonite and kaolinite, however, released some of the initially sorbed radionuclide with increasing contact time.

Jacobs and Tamura (1960, p. 208) consider ion exchange to be the dominant retention mechanism. The sorption curve that they obtained for illite could not be reconstructed on the basis of a single equilibrium coefficient. By using a second approximation in which a limited number of highly selective cesium exchange sites was available, a curve could be computed that matched the observed data.

The accessibility of the interlayer cations or cation positions for exchange reactions in a 10 A structure would be limited. Cesium sorption in a 10 A structure then must occur primarily at the edges of the clay platelets because the mineral structure is not free to expand in a hydrated system. With time some of the more accessible potassium in the interlayer position would be replaced by cesium

(Jacobs and Tamura, 1960, p. 209).

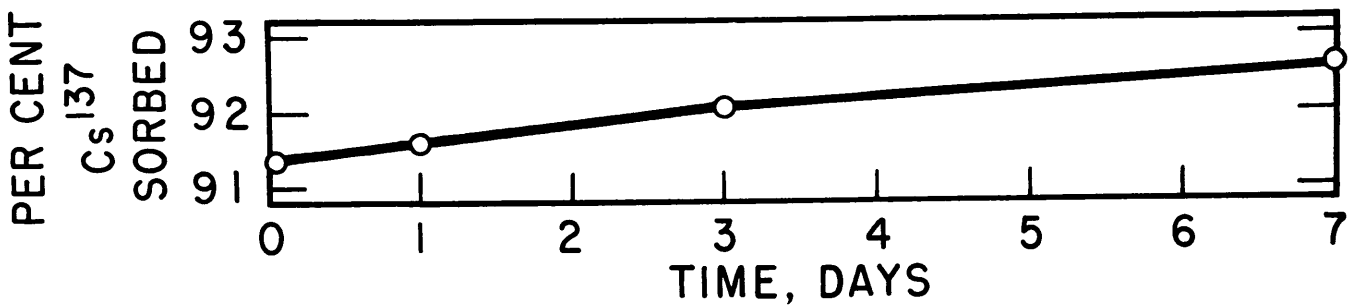
The percent of cesium-137 activity sorbed by the sediment did not appear to be particularly pH-sensitive over a wide range of values. Data presented by Reynolds and Clanton (1963, p. 133) indicate that changes in pH from 3 to 9 modified cesium-137 sorption values from 88 to 92 percent. At low pH levels the H^+ ion becomes a serious competitor for the exchange values but excessively high pH values will also destroy the clay structure (Anderson, 1961, p. 10).

Strontium sorption was highly sensitive to variations in pH. Clanton and Reynolds (1963, p. 133) report changes from 35 to 75 percent as the pH of the solution was varied from 3 to 11. At high H^+ ion concentrations the interlayer cations are displaced from the structure by the mass action effect of the highly competitive H^+ ions.

Cesium and potassium produce a collapsed 10 A structure. Strontium and calcium produce an expanded structure that requires two or more molecular layers of water to complete the crystal structure. The difference in sensitivity to changes in pH then reflects the inability of liquids and other cations to enter into the collapsed 10 A structure.

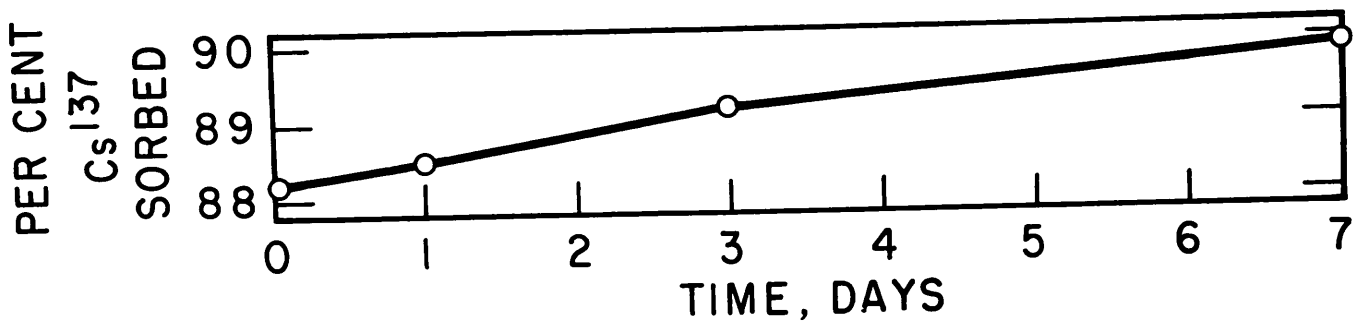
The average Cs^{137} sorption for samples with organic material removed and untreated samples is shown in Figure 17 and 18 respectively. The data indicate:

1. Sorption is highest in untreated samples; 91-93 percent in



1 Hour		7 Days
91.4%	Average	92.6%
89.4%	Minimum	91.3%
94.5%	Maximum	95.7%

FIGURE 17. AVERAGED CESIUM-137 SORPTION PERCENTAGES FOR 30 SAMPLES, UNTREATED



1 Hour		7 Days
88.2%	Average	89.9%
85.0%	Minimum	85.9%
91.7%	Maximum	92.4%

FIGURE 18. AVERAGED CESIUM-137 SORPTION PERCENTAGES FOR 30 SAMPLES, ORGANIC MATERIAL REMOVED

untreated vs. 88-90 percent in treated.

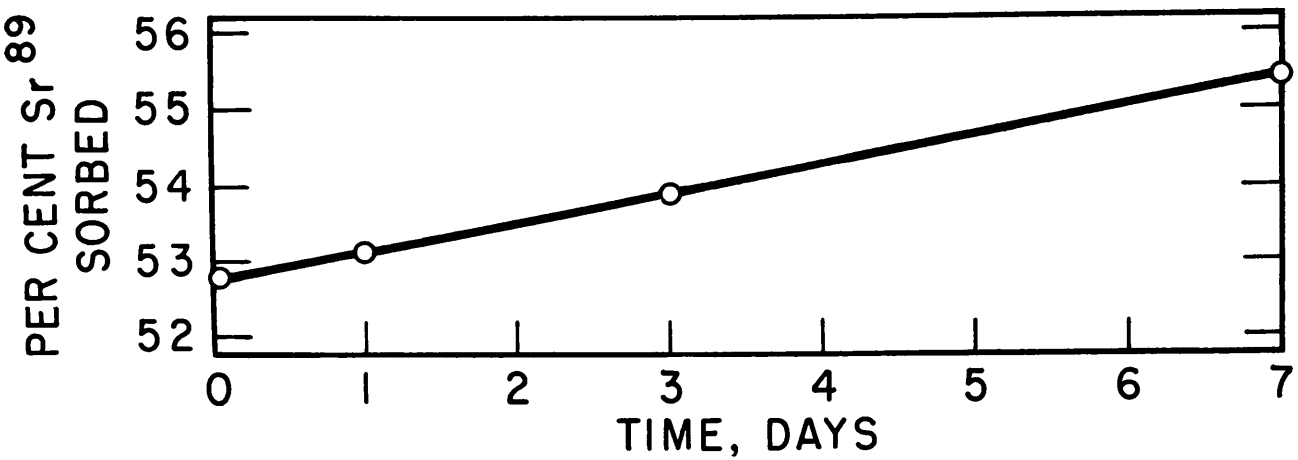
2. Sorption gradually increases during the seven day period.
3. The greatest rate of sorption occurs during the first hour of contact.
4. The organic material sorbed on the clay surfaces increases the over-all sorption capacity of the sediments.

Figures 19 and 20 show similar data for Sr-89. The most noticeable difference is the lower sorption values obtained with this cation. Untreated samples removed on the average 53-55 percent of the Sr-89; the treated samples removed 42-46 percent of the Sr-89.

Radionuclide Release

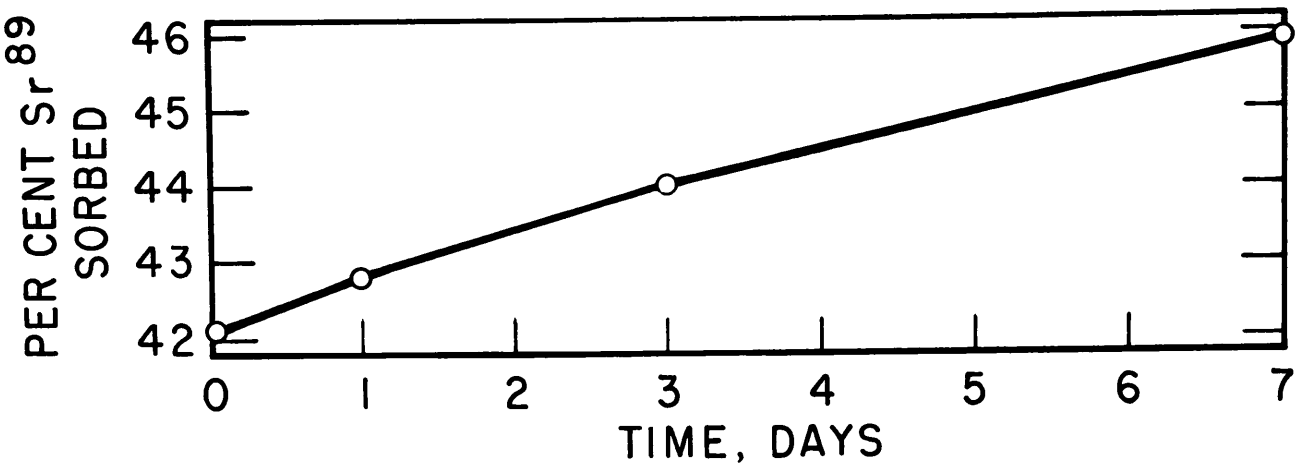
The number of competing ions and the extent of cation hydration in the interlayer position are the two most important criteria influencing the release of radionuclides from contaminated sediments. The extent to which radionuclides are sorbed by the sediments in a stream system depends primarily on the total number of ions competing for a given cation site within the clay structure. Obviously, then, this mass action effect will determine the probability and availability of a particular ion for a given cation site.

Even though ions are available to occupy the charged cation sites, some mechanism is required to effect the ion exchange reaction. If the clay particle has a hydrated structure with the interlayer cation hydrated by one or more molecular layers of water, the clay structure will be sufficiently expanded to permit the exchange of ions. If, however, the ion in the interlayer position is not hydrated



1 Hour		7 Days
52.8%	Average	55.4%
46.7%	Minimum	50.2%
58.0%	Maximum	61.6%

FIGURE 19. AVERAGED STRONTIUM-89 SORPTION PERCENTAGES FOR 25 SAMPLES, UNTREATED



1 Hour		7 Days
42.8%	Average	45.9%
34.0%	Minimum	36.1%
48.1%	Maximum	54.1%

FIGURE 20. AVERAGED STRONTIUM-89 SORPTION PERCENTAGES FOR 25 SAMPLES, ORGANIC MATERIAL REMOVED

and the clay structure is in the collapsed 10 A form, then there is no easy way for the competing ions to displace the entrapped ions.

Strontium sorbed in the clay structure would most probably be in the interlayer position and would be hydrated with two or more molecular layers of water. Such an expanded structure would allow easy access of calcium and magnesium ions to displace the strontium-89 ion. This mass action competition is responsible for the forty percent release of strontium-89 when the sediments were transferred from distilled water to river water. The lack of reaction by the cesium-137 contaminated sample when it was placed in river water is explained by the stronger cesium bond and by the limited number of hydrated cesium ions in the interlayer position. Then, too, the collapsed structure is not well suited for ion exchange reactions.

In the marine environment the competition for exchange sites is much more severe because of the mass action effect of the sodium. The ions in the sea water replaced over forty percent of both cesium-137 and strontium-89 sorbed on the sediments after these sediments were transferred from the fluvial environment into the lagoonal environment.

The release of the radionuclides as the contaminated sediments are brought into the marine environments creates a new series of problems, which will become increasingly severe to future generations.

Environments

Fluvial and marine environments are dynamic. Radionuclides present in the system will be sorbed or released in response to the

changes that occur in the environment.

The dynamic environment that a stream system represents is perhaps best indicated by stream discharge data. The variations in discharge that can be expected in the stream systems of Texas is well documented in the annual publication of the U.S. Geological Survey - Water Resources Division, "Water Resources Data for Texas - Part 1. Surface Water Records."

The dynamic conditions that exist in the Guadalupe River can be summarized by examining the discharge values reported for various gaging stations along this stream system. Gaging station 8-1655 (USGS, 1967, p. 379) is near the city of Hunt, Texas, and is about one-half mile below the confluence of the North and South Forks of the Guadalupe River. The total basin area that is drained by the stream at this point is calculated to be 276 square miles. The variations in daily discharge rate for the water-year 1966 lists a maximum discharge of 15,700 cfs, a minimum discharge of 15 cfs, and a mean daily discharge for the year of 100 cfs. However, since the time required for the exchange reaction is typically on the order of an hour or less, the extremes that occur at the time of flood crest or at periods of minimum discharge would give a greater insight to the problems of dilution and concentration. The maximum extreme for the year was 47,000 cfs; the minimum discharge was 14 cfs. The maximum extreme discharge known for this station since 1900 is 206,000 cfs; the minimum discharge is 6.9 cfs.

Gaging station 8-1675 (USGS, 1967, p. 382) is located near

Spring Branch, Texas. The area drained by the Guadalupe River at this location is calculated to be 1,282 square miles. The maximum discharge for the year 1966 was 8,250 cfs; the minimum discharge was 34 cfs with a mean daily discharge of 238 cfs. During its 44-year history, this station has recorded an extreme maximum discharge of 121,000 cfs and several extended periods when no flow could be detected.

Gaging Station 8-1765 (USGS, 1967, p. 397) is located in Victoria, Texas. The drainage basin of the Guadalupe River at this location is calculated to contain 5,161 square miles. The maximum discharge during the year 1966 for the Guadalupe River at this location was 9,420 cfs; a minimum discharge of 511 cfs was recorded with a mean daily discharge for the year of 1,551 cfs. The extreme maximum discharge known from this location is 179,000 cfs; the minimum discharge known is 14 cfs.

These variations in stream flow at each station can be quite enlightening when one calculates the difference between the various measured discharge rates. The gaging station at Hunt, Texas, had a maximum/minimum discharge rate that varied by a factor of 1,047. The maximum/mean discharge rate varied by a factor of 157. The station at Spring Branch, Texas, had a maximum/minimum discharge rate that varied by a factor of 243; the maximum/mean varied by a factor of 35. At Victoria, Texas, the maximum/minimum and maximum/mean discharge rates varied by a factor of 18 and 6 respectively.

The above data were calculated on the daily discharge rates for

the 1966 water year. It would appear that one could expect variations in flow rates ranging from one to three orders of magnitude.

Stout, Bentz and Ingram (1961, p. 145-153) list suspended silt values for the Guadalupe River at the Spring Branch and Victoria locations. The records are complete for seventeen and fourteen years respectively. The maximum silt load during a one month period for the Spring Branch location was 688,220 tons for the month of September 1952. The minimum silt load of 10 tons occurred in the month of October 1961. The amount of material in suspension (dry weight) ranged from 0.001 to 0.561 percent. The Guadalupe River at Victoria had a maximum suspended silt load of 486,558 tons for May 1957. A minimum of 117 tons was observed for June of 1956. Maximum and minimum material in suspension (dry weight) ranged from 0.002 to 0.141 percent.

At both sampling locations the maximum stream discharge reported in monthly increments does not correlate with the maximum percentage of suspended material and/or maximum tonnage of silt load. The fluvial environment is dynamic and complex. A simple extrapolation cannot adequately predict the reactions that will occur under the diverse flow rates.

CONCLUSIONS

1. The clay mineral assemblage in the bed load of the Guadalupe River and San Antonio Bay cannot be characterized as discrete clay minerals but is composed of a mixed-layer clay mineral complex of poor crystallinity. Minor features on the x-ray diffraction patterns indicate the presence of discrete clay species, but these too are badly degraded.

2. The low x-ray diffraction intensities observed from the sediment samples can only be explained by the presence of a constituent or constituents that are amorphous to x-radiation. The amorphous material must either be a skeletal clay structure or an amorphous form of SiO_2 or perhaps both.

3. Ion exchange capacity values indicate that the response of the amorphous material to the 1N barium chloride treatment is quite low. K_d values, however, indicate that this material sorbs the trace radionuclides almost as well as do the more crystalline clay minerals farther down river.

4. The highest percentage of radionuclide sorption took place on sediments containing the naturally occurring organic fraction. The organic constituent with its higher sorption capacity was responsible for the observed increase.

5. The sorption of radionuclides by sediments is not a reaction that can be directly related to the ion exchange capacity of the sediments. No sequential correlation exists between the amount of radionuclide sorbed and the ion exchange capacity as determined or as

recalculated for the samples. Ion exchange capacity measurements are a poor indicator of the ability of a material to sorb a particular radionuclide.

6. This study indicated that the percentage of radionuclides sorbed by the sediments did not change materially throughout the length of the Guadalupe River and San Antonio Bay. The observed variations in mineralogy of the samples did not appear to have any effect on K_d values.

7. It is possible to predict the reactions of the radionuclides as they pass through the river and lagoon environments using a laboratory study as a basis for the extrapolation. However, the prediction will be valid only if sufficient samples of water and sediment are available to characterize the environments.

8. Radionuclides present in the system will be sorbed or released in response to changes that occur in the fluvial and marine environments. Exchange reactions can be expected at times of flooding, under conditions of drought, where differences in lithology add a competing cation, in areas of municipal and industrial pollution and when the stream discharges into the marine environment.

9. The rate of reaction for both sorption and release of the radionuclides is rapid and for all practical considerations complete within the first hour. This high rate of reaction is perhaps the most critical consideration in radioactive waste disposal.

10. Both cesium-137 and strontium-89 were sorbed in the fluvial environment only to be released when the contaminated sediment entered

the marine environment. Such reactions disperse the radionuclides and extend the area of contamination.

APPENDIX

Sample Locations

General Highway Maps from the Texas Highway Department were used to determine sample locations. The 1937 Geologic Map of Texas by the United States Geological Survey served as a basis for the geologic units referred to in this report. The stratigraphic names refer to the units cropping out along the river course at the sample locations and not to the actual samples.

C-1 Kerr county; east of Hunt 0.6 miles where Highway 39 crosses the Guadalupe River.

Cretaceous, Comanche series, Trinity group.

C-3 Kerr county; west of Comfort 1.3 miles at the crossing of Mill Road and the Guadalupe River

Cretaceous, Comanche series, Trinity group.

C-5 Kendall county; south 0.8 miles from the southern junction of Highways 473 and 1376 near Sisterdale where Highway 1376 crosses the Guadalupe River.

Cretaceous, Comanche series, Trinity group.

C-7 Kendall county; north of Bergheim about 5 miles where surfaced road crosses the Guadalupe River.

Cretaceous, Comanche series, Trinity group.

C-8 Comal county; southeast of Spring Branch about 2 miles where Highway 311 crosses the Guadalupe River

Cretaceous, Comanche series, Trinity group.

C-9 Comal county; north of the New Braunfels city limits about 4 miles along River Road at the second bridge over the Guadalupe River.

Cretaceous, Comanche series, Fredricksburg group.

C-11 Guadalupe county; southeast of New Braunfels about 5 miles in Lake Dunlop on the Guadalupe River.

Cretaceous, Gulf series, Taylor group.

C-12 Guadalupe county; from the Randolph Air Force Base Camp on Lake McQueeney.

Cretaceous, Gulf series, Navarro group, Corsicana marl.

C-13 Guadalupe county; below the Old Bridge at McQueeney.

Cretaceous, Gulf series, Navarro group, Kemp clay.

C-14 Guadalupe county; west of Seguin about 3 miles where Highway 1620 crosses the Guadalupe River.

Tertiary, Eocene, Midway group, Wills Point clay.

C-16 Guadalupe county; south of Highway 90A and 466 road junction about 3 miles where Highway 466 crosses the Guadalupe River

Tertiary, Eocene, Wilcox group.

C-17 Gonzales county; west of Belmont 1.3 miles where Highway 80 crosses the Guadalupe River.

Tertiary, Eocene, Claiborne group, Carrizo sand.

C-18 Gonzales county; Lake Gonzales near Wade Dam.

Tertiary, Eocene, Claiborne group, Queen City.

C-19A Gonzales county; about 8 miles south of Gonzales on Highway 183, turn off on unmarked pasture road and go about one mile to the Guadalupe River.
Tertiary, Eocene, Jackson group.

C-19B Gonzales county; east from Hamon about 3.5 miles on an unnamed dirt road to the abandoned river crossing.
Tertiary, Miocene, Catahoula Tuff.

C-20 DeWitt county; west of Hochheim about one mile where Highway 183 crosses the Guadalupe River.
Tertiary, Miocene, Oakville.

C-21 DeWitt county; northwest of Cuero about 4 miles where Highway 776 crosses the Guadalupe River.
Tertiary, Miocene, Oakville.

C-22 DeWitt county; south of Cuero about 3 miles where Highway 236 crosses the Guadalupe River.
Tertiary, Miocene, Lagarto clay.

C-24 Victoria county; west of Nursery about 3 miles where Highway 447 crosses the Guadalupe River.
Tertiary, Pliocene, Goliad sand.

C-25 Victoria county; boat ramp in Victoria City Park.
Quaternary, Pleistocene, Beaumont clay.

C-26 Victoria county; southeast of Victoria about 10 miles, west on unnamed dirt road about 3 miles to the old Swinging Bridge over the Guadalupe River.
Quaternary, Pleistocene, Beaumont clay.

C-27 Calhoun county; crossing of Highway 35 and the Guadalupe River.

Quaternary, Pleistocene, Beaumont clay.

C-28 San Antonio Bay; sample collected about 2 miles south of where the Guadalupe River empties into Guadalupe Bay.

Quaternary, Recent, Alluvium.

C-29 to C-35 San Antonio Bay; samples collected at one-half mile intervals along a line 0.5 miles west of longitude 96°45'W.

Quaternary, Recent, Alluvium.

C-36 San Antonio Bay; sample collected about 1.5 miles east of Hoopers Landing along a line 0.5 miles west of longitude 96°45'W.

Quaternary, Recent, Alluvium.

C-37 to C-45 San Antonio Bay; samples collected at one-half mile intervals along a line 0.5 miles west of longitude 96°45'W.

Quaternary, Recent, Alluvium.

C-46 San Antonio Bay; south of Buoy 51 in the Intracoastal Canal about 0.1 miles. (Both C-45 and C-46 are from the spoil areas of the Intracoastal Canal).

Quaternary, Recent, Alluvium.

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